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LXXVI. *The Quantum Theory of Radiation.*
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Introduction.

IN the attempts to give a theoretical interpretation of the mechanism of interaction between radiation and matter, two apparently contradictory aspects of this mechanism have been disclosed. On the one hand, the phenomena of interference, on which the action of all optical instruments essentially depends, claim an aspect of continuity of the same character as that involved in the wave theory of light, especially developed on the basis of the laws of classical electrodynamics. On the other hand, the exchange of energy and momentum between matter and radiation, on which the observation of optical phenomena ultimately depends, claims essentially discontinuous features. These have even led to the introduction of the theory of light-quanta, which in its most extreme form denies the wave constitution of light. At the present state of science it does not seem possible to avoid the formal character of the quantum theory which is shown by the fact that the interpretation of atomic phenomena does not involve a description of the mechanism of the discontinuous processes, which in the quantum theory of spectra are designated as transitions between stationary states of the atom. On the correspondence principle it seems

* Communicated by the Authors.

nevertheless possible, as it will be attempted to show in this paper, to arrive at a consistent description of optical phenomena by connecting the discontinuous effects occurring in atoms with the continuous radiation field in a somewhat different manner from what is usually done. The essentially new assumption introduced in § 2 that the atom, even before a process of transition between two stationary states takes place, is capable of communication with distant atoms through a virtual radiation field, is due to Slater*. Originally his endeavour was in this way to obtain a harmony between the physical pictures of the electro-dynamical theory of light and the theory of light-quanta by coupling transitions of emission and absorption of communicating atoms together in pairs. It was pointed out by Kramers, however, that instead of suggesting an intimate coupling between these processes, the idea just mentioned leads rather to the assumption of a greater independence between transition processes in distant atoms than hitherto perceived. The present paper is the result of a mutual discussion between the authors concerning the possible importance of these assumptions for the elaboration of the quantum theory, and may in various respects be considered as a supplement to the first part of a recent treatise by Bohr, dealing with the principles of the quantum theory, in which several of the problems dealt with here are treated more fully †.

§ 1. *Principles of the Quantum Theory.*

The electromagnetic theory of light not only gives a wonderfully adequate picture of the propagation of radiation through free space, but has also to a wide extent shown itself adapted for the interpretation of the phenomena connected with the interaction of radiation and matter. Thus a general description of the phenomena of emission, absorption, refraction, scattering, and dispersion of light may be obtained on the assumption that the atoms contain electrified particles which can perform harmonic oscillations round positions of stable equilibrium, and which will exchange energy and momentum with the radiation fields according to the classical laws of electro-dynamics. On the other

* J. C. Slater, 'Nature,' March 1st, 1924, p. 307.

† N. Bohr, *Zeitschr. für Phys.* xiii. p. 117 (1923). An English translation has recently appeared in the Publications of the Cambridge Philosophical Society under the title: "On the application of the Quantum Theory to atomic structure. I.: The fundamental postulates of the quantum theory." This treatise, which also contains more detailed references to the literature, will in the following be quoted as "P. Q. T."

hand, it is well known that these phenomena exhibit a number of features which are contradictory to the consequences of the classical electrodynamical theory. The first phenomenon where such contradictions were firmly established was the law of temperature radiation. Starting from the classical conception of emission and absorption of radiation by a particle performing harmonic oscillations, Planck found that, in order to obtain agreement with the experiments on temperature radiation, it was necessary to introduce the auxiliary assumption that in a statistical distribution only certain states of the oscillating particles have to be taken into account. For these distinguished states the energy was found to be equal to a multiple of the quantum $h\omega$, where ω is the natural frequency of the oscillator and h is a universal constant. Independent of radiation phenomena, this result obtained, as Einstein pointed out, a direct support from experiments on the specific heat of solids. At the same time, this author put forward his well-known theory of "light-quanta," according to which radiation should not be propagated through space as continuous trains of waves in the classical theory of light, but as entities, each of which contains the energy $h\nu$, concentrated in a minute volume, where h is Planck's constant and ν the quantity which in the classical picture is described as the number of waves passing in unit time. Although the great heuristic value of this hypothesis is shown by the confirmation of Einstein's predictions concerning the photoelectric phenomenon, still the theory of light-quanta can obviously not be considered as a satisfactory solution of the problem of light propagation. This is clear even from the fact that the radiation "frequency" ν appearing in the theory is defined by experiments on interference phenomena which apparently demand for their interpretation a wave constitution of light.

In spite of the fundamental difficulties involved in the ideas of the quantum theory, it has nevertheless been possible to a certain extent to apply these conceptions, combined with information on the structure of the atom derived from other sources, to the interpretation of the results of investigations of the emission and absorption spectra of the elements. This interpretation is based on the fundamental postulate: that an atom possesses a number of distinguished states, the so-called "stationary states," which are supposed to possess a remarkable stability, for which no interpretation can be derived from the concepts of classical electrodynamics. This stability comes to light in the circumstance that any change of the state of the atom must consist of a

complete process of transition from one of these stationary states to another. The postulate obtains a connexion with optical phenomena through the further assumption that when a transition between two stationary states is accompanied by emission of radiation, this consists of a train of harmonic waves, whose frequency is given by the relation

$$h\nu = E_1 - E_2, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where E_1 and E_2 are the values of the energy of the atom in the initial and in the final state of the process respectively. Inversely it is assumed that the reversed process of transition can take place by illumination with light with this same frequency. The applicability of these assumptions to the interpretation of the spectra of the elements is essentially due to the fact that it has been found possible in many cases to fix the energy in the stationary states of an isolated atom by means of simple rules referring to motions which with a high approximation obey the ordinary laws of electrodynamics (P.Q.T., Ch. I., § 2). The concepts of this theory, however, do not allow us to describe the details of the mechanism underlying the process of transition between the various stationary states.

At the present state of science it seems necessary, as regards the occurrence of transition processes, to content ourselves with considerations of probability. Such considerations have been introduced by Einstein*, who has shown how a remarkably simple deduction of Planck's law of temperature radiation can be obtained by assuming that an atom in a given stationary state may possess a certain probability of a "spontaneous" transition in unit time to a stationary state of smaller energy content, and that in addition an atom, by illumination with external radiation of suitable frequency, may acquire a certain probability of performing an "induced" transition to another stationary state with higher or smaller energy content. In connexion with the conditions of thermal equilibrium between radiation and matter, Einstein further arrived at the conclusion that the exchange of energy by the transition process is accompanied by an exchange of momentum of the amount $h\nu/c$, just as would be the case if the transition were accompanied by the starting or stopping of a small entity moving with the velocity of light c and containing the energy $h\nu$. He concluded that the direction of this momentum for the induced transitions is the same as the direction of

* A. Einstein, *Physikalische Zeitschrift*, xviii. p. 121 (1917).

propagation of the illuminating light-waves, but that for the spontaneous transitions the direction of the impulse is distributed according to probability laws. These results, which were considered as an argument for ascribing a certain physical reality to the theory of light-quanta, have recently found an important application in explaining the remarkable phenomena of the change of wave-length of radiation scattered by free electrons brought to light by A. H. Compton's * investigation on X-ray scattering. The application of probability considerations to the problem of temperature equilibrium between free electrons and radiation suggested by this discovery has recently been successfully treated by Pauli †, and the formal analogy of his results with the laws governing transition processes between stationary states of atoms has been emphasized by Einstein and Ehrenfest ‡.

In spite of the fundamental departure of the quantum theory of atomic processes from a picture based on the ordinary concepts of electrodynamics, the former must in a certain sense ultimately appear as a natural generalization of the latter. This is evident from the condition that in the limit, where we consider processes which depend on the statistical behaviour of a large number of atoms, and which involve stationary states where the difference between neighbouring stationary states is comparatively little, the classical theory leads to conclusions in agreement with the experiments. In the case of emission and absorption of spectral lines, this connexion between the two theories has led to the establishment of the "correspondence principle," which postulates a general conjugation of each of the various possible transitions between stationary states with one of the harmonic oscillation components in which the electrical moment of the atom, considered as a function of the time, can be resolved (P. Q. T., Ch. II., § 2). This principle has afforded a basis for an estimation of probabilities of transition, and thereby for bringing the problem of intensities and polarization of spectral lines in close connexion with the motion of the electrons in the atom.

The correspondence principle has led to comparing the reaction of an atom on a field of radiation with the reaction on such a field which, according to the classical theory of electrodynamics, should be expected from a set of "virtual" harmonic

* A. H. Compton, *Phys. Rev.* xxi. p. 483 (1923). See also P. Debye, *Physikalische Zeitschrift*, xxiv. p. 161 (1923).

† W. Pauli, *Zeitschrift für Phys.* xviii. p. 272 (1923).

‡ A. Einstein and P. Ehrenfest, *Zeitschr. für Phys.* xiv. p. 301 (1923).

oscillators with frequencies equal to those determined by the equation (1) for the various possible transitions between stationary states (P.Q.T., Ch. III., § 3). Such a picture has been used by Ladenburg* in an attempt to connect the experimental results on dispersion quantitatively with considerations on the probability of transitions between stationary states. Also in the phenomenon of interaction between free electrons and radiation, the possibility of applying similar considerations is suggested by the analogy, emphasized by Compton, between the change of wave-length of the scattered rays and the classical Doppler effect of radiation from a moving source.

Although the correspondence principle makes it possible through the estimation of probabilities of transition to draw conclusions about the mean time which an atom remains in a given stationary state, great difficulties have been involved in the problem of the time-interval in which emission of radiation connected with the transition takes place. In fact, together with other well-known paradoxes of the quantum theory, the latter difficulty has strengthened the doubt, expressed from various sides†, whether the detailed interpretation of the interaction between matter and radiation can be given at all in terms of a causal description in space and time of the kind hitherto used for the interpretation of natural phenomena (P. Q. T., Ch. III., § 1). Without in any way removing the formal character of the theory, it nevertheless appears, as mentioned in the introduction, that a definite advance as regards the interpretation of the observable radiation phenomena may be made by connecting these phenomena with the stationary states and the transitions between them in a way somewhat different from that hitherto followed.

§ 2. *Radiation and Transition Processes.*

We will assume that a given atom in a certain stationary state will communicate continually with other atoms through a time-spatial mechanism which is virtually equivalent with the field of radiation which on the classical theory would originate from the virtual harmonic oscillators corresponding with the various possible transitions to other stationary states. Further, we will assume that the occurrence of

* R. Ladenburg, *Zeitschr. für Phys.* iv. p. 451 (1921). See also R. Ladenburg and P. Reiche, *Naturwissenschaften*, xi. p. 584 (1923).

† Such a view has perhaps for the first time been clearly expressed by O. W. Richardson, 'The Electron Theory of Matter,' 2nd edition, p. 507, Cambridge 1916.

transition processes for the given atom itself, as well as for the other atoms with which it is in mutual communication, is connected with this mechanism by probability laws which are analogous to those which in Einstein's theory hold for the induced transitions between stationary states when illuminated by radiation. On the one hand, the transitions which in this theory are designated as spontaneous are, on our view, considered as induced by the virtual field of radiation which is connected with the virtual harmonic oscillators conjugated with the motion of the atom itself. On the other hand, the induced transitions of Einstein's theory occur in consequence of the virtual radiation in the surrounding space due to other atoms.

While these assumptions do not involve any change in the connexion between the structure of the atom and the frequency, intensity, and polarization of the spectral lines derived by means of the relation (1) and of the correspondence principle, they lead to a picture as regards the time-spatial occurrence of the various transition processes on which the observations of the optical phenomena ultimately depend which in an essential respect differs from the usual concepts. In fact, the occurrence of a certain transition in a given atom will depend on the initial stationary state of this atom itself and on the states of the atoms with which it is in communication through the virtual radiation field, but not on the occurrence of transition processes in the latter atoms.

On the one hand it will be seen that our view, in the limit where successive stationary states differ only little from each other, leads to a connexion between the virtual radiation field and the motion of the particles in the atom which gradually merges into that claimed by the classical radiation theory. In fact neither the motion nor the constitution of the radiation field will in this limit undergo essential changes through the transitions between stationary states. As regards the occurrence of transitions, which is the essential feature of the quantum theory, we abandon on the other hand any attempt at a causal connexion between the transitions in distant atoms, and especially a direct application of the principles of conservation of energy and momentum, so characteristic for the classical theories. The application of these principles to the interaction between individual atomic systems is, on our view, limited to interactions which take place when the atoms are so close that the forces which would be connected with the radiation field on the classical theory are small compared with the conservative parts of the fields of force originating from the electric

charges in the atom. Interactions of this type, which may be termed "collisions," offer, as is well known, remarkable illustrations of the stability of stationary states postulated in the quantum theory. In fact, an analysis of the experimental results based on the theory of conservation of energy and momentum is in agreement with the view that the colliding atoms before as well as after the process will always find themselves in stationary states (P. Q. T., Ch. I., § 4)*. By interaction between atoms at greater distances from each other, where according to the classical theory of radiation there would be no question of simultaneous mutual action, we shall assume an independence of the individual transition processes, which stands in striking contrast to the classical claim of conservation of energy and momentum. Thus we assume that an induced transition in an atom is not directly caused by a transition in a distant atom for which the energy difference between the initial and the final stationary state is the same. On the contrary, an atom which has contributed to the induction of a certain transition in a distant atom through the virtual radiation field conjugated with the virtual harmonic oscillator corresponding with one of the possible transitions to other stationary states, may nevertheless itself ultimately perform another of these transitions.

At present there is unfortunately no experimental evidence at hand which allows to test these ideas, but it may be emphasized that the degree of independence of the transition processes assumed here would seem the only consistent way of describing the interaction between radiation and atoms

* These considerations hold obviously only in so far as the radiation connected with the collisions can be neglected. Although in many cases the energy of this radiation is very small, its occurrence might be of essential importance. This has been emphasized by Franck in connexion with the explanation of Ramsauer's important results regarding collisions between atoms and slow electrons (*Ann. d. Phys.* lxiv. p. 513, lxvi. p. 546 (1922)), from which it seems to follow that in certain cases the electron can pass freely through the atom, without being influenced by its presence. In fact, if in these "collisions" a change in the motion of the electron actually took place, the classical theory would involve so large a radiation, that a rational conjugation of the radiation with the possible transition processes, as claimed by the correspondence principle, could hardly be established (compare F. Hund, *Zs. für Phys.* xiii. p. 241, 1923). On the view presented in this paper, such an explanation might on the one hand be regarded as the more natural, since the origin of radiation is not directly sought in the occurrence of transitions but in the motion of the electron. On the other hand, it must be remembered that we are here dealing with a case where, on account of the large magnitude of the classical reaction of radiation, the theory does not allow a sharp distinction between stationary motion and transition processes.

by a theory involving probability considerations. This independence reduces not only conservation of energy to a statistical law, but also conservation of momentum. Just as we assume that any transition process induced by radiation is accompanied by a change of energy of the atom of the amount $h\nu$, we shall assume, following Einstein, that any such process is also accompanied by a change of momentum of the atom of an amount $h\nu/c$. If the transition is induced by virtual radiation fields from distant atoms, the direction of this momentum is the same as that of the wave propagation in this virtual field. In case of a transition by its own virtual radiation, we shall naturally assume that the change of momentum is distributed according to probability laws in such a way that changes of momentum due to the transitions in other atoms are statistically compensated for any direction in space.

The cause of the observed statistical conservation of energy and momentum we shall not seek in any departure from the electrodynamic theory of light as regards the laws of propagation of radiation in free space, but in the peculiarities of the interaction between the virtual field of radiation and the illuminated atoms. In fact, we shall assume that these atoms will act as secondary sources of virtual wave radiation which interferes with the incident radiation. If the frequency of the incident waves coincides closely with the frequency of one of the virtual harmonic oscillators corresponding to the various possible transitions, the amplitudes of the secondary waves will be especially large, and these waves will possess such phase relations with the incident waves that they will diminish or augment the intensity of the virtual radiation field, and thereby weaken or strengthen its power of inducing transitions in other atoms. Whether it is a diminishing or an augmentation of the intensity which takes place, will depend on whether the virtual harmonic oscillator, which is called into play by the incident radiation, corresponds with a transition by which the energy of the atom is increased or diminished respectively. It will be seen that this view is closely related to the ideas which led Einstein to introduce probabilities of two kinds of induced transitions between stationary states corresponding with an increase or decrease of the energy of the atom respectively. In spite of the time-spatial separation of the processes of absorption and emission of radiation characteristic for the quantum theory, we may nevertheless expect, on our view, a far-reaching analogy with the classical theory of electrodynamics as regards the interaction of the virtual radiation field and the

virtual harmonic oscillators conjugated with the motion of the atom. It seems actually possible, guided by this analogy, to establish a consistent and fairly complete description of the general optical phenomena accompanying the propagation of light through a material medium, which accounts at the same time for the close connexion of these phenomena with the spectra of the atoms of the medium.

§ 3. *Capacity of Interference of Spectral Lines.*

Before we enter more closely on the general problem of the reaction of atoms on a virtual radiation field, responsible for the phenomena accompanying the propagation of light through material media, we shall here briefly consider the properties of the field originating from a single atom, as far as they are connected with the capacity of interference of light from one and the same source. The constitution of this field must obviously not be sought in the peculiarities of the transition processes themselves, the duration of which we shall assume at any rate not to be large compared with the period of the corresponding harmonic component in the motion of the atom. These processes will, on our view, simply mark the termination of the time-interval in which the atom will be able to communicate with other atoms through the corresponding virtual oscillator. An upper limit of the capacity of interference, however, will clearly be given by the mean time interval in which the atom remains in the stationary state representing the initial state of the transition under consideration. The estimation of the time of duration of states based on the correspondence principle has obtained a general confirmation from the well-known beautiful experiments on the duration of the luminosity of high speed atoms emerging from a luminescent discharge into a high vacuum. (Compare P. Q. T., Ch. II., § 4.) On the present point of view these experiments obtain a very simple interpretation. In fact it will be seen that on this view the variation of the luminosity along the path of the atoms will not depend on the peculiarity of the transitions, but only on the relative number of atoms in the various stationary states in the different parts of the path. If all the emerging atoms have the same speed and are initially in the same state, we must thus expect that for any spectral line conjugated with a transition from this state the luminosity will decrease exponentially along the path at one and the same rate. At present the experimental material at hand is hardly sufficient to test these considerations.

When we ask for the capacity of interference of spectral lines, determined by optical apparatus, the mean time of duration of the stationary states will certainly constitute an upper limit for this capacity, but it must be remembered that the sharpness of a given spectral line which is due to the statistical result of the action from a large number of atoms will depend not only on the lengths of the individual wave trains terminated by the transition processes, but clearly also on any uncertainty in the definition of the frequency of these waves. In view of the way this frequency through relation (1) is related to the energy in the stationary states, it is of interest to note that the above-mentioned upper limit of capacity of interference may be brought in close connexion with the limit of definition of the motion and of the energy in the stationary states. In fact, the postulate of the stability of stationary states imposes an *a priori* limit to the accuracy with which the motion in these states can be described by means of classical electrodynamics, a limit which on our picture is directly involved in the assumption that the virtual radiation field is not accompanied by a continuous change in the motion of the atom, but only acts by its induction of transitions involving finite changes of the energy and the momentum of the atom (P. Q. T., Ch. II., § 4). In the limiting region where the motions in the two stationary states involved in the transition process differ only comparatively little from each other, the upper limit of capacity of interference of the individual wave trains coincides with the limit of definition of the frequency of the radiation determined by (1), if the influence of the lack of definition of the energy in the two states is treated as independent errors. In the general case where the motions in these states may differ considerably from each other, the upper limit of the capacity of interference of the wave trains is closely related with the definition of the motion in the stationary state which forms the starting point of the transition process. Also here we may, however, expect that the observable sharpness of the spectral lines will be determined according to relation (1) by adding the effect of any possible lack of definition of the energy in the stationary state terminating the transition process to the effect of the lack of definition in the starting state in a similar way as independent errors. Just this influence of the lack of definition of both stationary states on the sharpness of a spectral line makes it possible to ensure the reciprocity which will exist between the constitution of a line when appearing in an emission and in an absorption spectrum, and which is claimed by the

condition for thermal equilibrium expressed by Kirchhoff's law. In this connexion it may be remembered how the apparent deviations from this law exhibited by the remarkable difference often shown by the structure of the emission and the absorption spectra of an element as regards the number of lines present are directly accounted for on the quantum theory when account is taken of the difference in the statistical distributions of the atoms over the various stationary states under different external conditions.

A problem closely related to the sharpness of spectral lines originating from atoms under constant external conditions, is the problem of the spectrum to be expected from atoms under the influence of external forces which vary considerably within a time-interval of the same order of magnitude as the mean duration of the stationary states. Such a problem is met with in certain of the experiments by Stark on the influence of electric fields on spectral lines. In these experiments the emitting atoms move with large velocities, and the time-intervals in which they pass between two points where the intensity of the electric field differs very much, are only a small fraction of the mean time of duration of the stationary states connected with the investigated spectral lines. Nevertheless Stark found that, except for a Doppler effect of the usual kind, the radiation from the moving atoms was influenced by the electric field at any point of the path in the same way as the radiation from resting atoms subject to the constant action of the field at this point. While, as emphasized by various authors*, the interpretation of this result obviously presents difficulty on the usual quantum theory description of the connexion between radiation and transition processes, it is clear that Stark's results are in conformity with the picture adopted in this paper. In fact, during the passing of the atoms through the field, the motion in the stationary states changes in a continuous way, and in consequence also the virtual harmonic oscillators corresponding with the possible transitions. The effect of the virtual radiation field originating from the moving atoms will therefore not be different from that which would occur if the atoms along their whole path had moved in a field of constant intensity, at any rate if—as in Stark's experiments—the radiation originating from the other parts of their paths is prevented from reaching those parts of the apparatus on which the observation of the phenomenon depends. In a

* Compare K. Försterling, *Zeitschr. für Phys.* x. p. 387 (1922), A. J. Deupster, *Astrophys. Journ.* lvii. p. 193 (1923).

problem of this kind it will also be seen how a far reaching reciprocity in the observable phenomena of emission and absorption is ensured on account of the symmetry exhibited by our picture as regards the coupling of the radiation field with the transition processes in the one or in the other direction.

§ 4. *Quantum Theory of Spectra and Optical Phenomena.*

Although on the quantum theory the observation of the optical phenomena ultimately depends on discontinuous transition processes, an adequate interpretation of these phenomena must, as already emphasized in the introduction, nevertheless involve an element of continuity similar to that exhibited by the classical electrodynamical theory of the propagation of light through material media. On this theory the phenomena of reflexion, refraction, and dispersion are attributed to a scattering of light by the atom due to the forced vibration in the individual electric particles, set up by the electromagnetic forces of the radiation field. The postulate of the stability of stationary states might at first sight seem to involve a fundamental difficulty on this point. The contrast, however, was to a certain extent bridged over by the correspondence principle, which, as mentioned in § 1, led to comparing the reaction of an atom on a radiation field with the scattering which, according to the classical theory, would arise from a set of virtual harmonic oscillators conjugated with the various possible transitions. It must still be remembered that the analogy between the classical theory and the quantum theory as formulated through the correspondence principle is of an essentially formal character, which is especially illustrated by the fact that on the quantum theory the absorption and emission of radiation are coupled to different processes of transition, and thereby to different virtual oscillators. Just this point, however, which is so essential for the interpretation of the experimental results on emission and absorption spectra, seems to afford a guidance as regards the way in which the scattering phenomena are related with the activity of the virtual oscillators concerning emission and absorption of radiation. In a later paper it is hoped to show how on the present view a quantitative theory of dispersion resembling Ladenburg's theory can be established*. Here we shall confine ourselves to emphasizing once more the continuous character of the optical phenomena,

* *Note added during the proof.* The outline of such a theory is briefly described by Kramers in a letter to 'Nature' published in April.

which seemingly does not permit an interpretation based on a simple causal connexion with transition processes in the propagating medium.

An instructive example of these considerations is offered by the experiments on absorption spectra. In fact, the pronounced absorption by monatomic vapours for light of frequencies coinciding with certain lines in the emission spectra of the atoms strictly cannot be said, as often done for brevity, to be caused by the transition processes which take place in the atoms of the vapour induced by wave trains in the incident radiation possessing the frequencies of the absorption lines. The appearance of these lines in the spectro-scope is due to the decrease of the intensity of the incident waves in consequence of the peculiarities of the secondary spherical wavelets set up by each of the illuminated atoms, while the induced transitions appear only as an accompanying effect by which a statistical conservation of energy is ensured. The presence of the secondary coherent wave-trains is at the same time responsible for the anomalous dispersion connected with the absorption lines, and is especially clearly shown by the phenomenon, discovered by Wood*, of selective reflexion from the wall of a vessel containing metallic vapour under sufficiently high pressure. The occurrence of induced transitions between stationary states is on the other hand directly observed in the fluorescent radiation, which for an essential part originates from the presence of a small number of atoms which through the illumination have been transferred to a stationary state of higher energy. As is well known, the fluorescent radiation can be suppressed through the admixture of foreign gases. As regards the part played by atoms in the higher stationary states this phenomenon is explained by collisions which cause a considerable increase of the probability of the atoms to return into their normal state. At the same time any part of the fluorescent radiation due to the coherent wavelets will, through the admixture of foreign gases, just as the phenomena of absorption, dispersion, and reflexion, undergo such changes as can be brought in connexion with a broadening of the spectral lines†. It will be seen that a view on absorption phenomena differing essentially from that just described can hardly be maintained, if it can be shown that the selective absorption of spectral lines is a phenomenon qualitatively independent of the intensity of the

* R. W. Wood, *Phil. Mag.* xxiii, p. 689 (1915).

† See for instance Chr. Füchtbauer and G. Joos, *Physik. Zeitschr.* xxiii, p. 73 (1922).

source of radiation, in a similar way to what has already been found to be the case for the usual phenomena of reflexion and refraction, whose transitions in the medium do not occur to a similar extent (compare P. Q. T., Ch. III., § 3).

Another interesting example is offered by the theory of the scattering of light by free electrons. As has been shown by Compton by means of reflexion of X-rays from crystals, this scattering is accompanied by a change of frequency, different in different directions, and corresponding with the constitution of the radiation which on the classical theory would be emitted by an imaginary moving source. As mentioned, Compton has reached a formal interpretation of this effect on the theory of light-quanta by assuming that the electron may take up a quantum of the incident light and simultaneously re-emit a light-quantum in some other direction. By this process the electron acquires a velocity in a certain direction, which is determined, just as the frequency of the re-emitted light, by the laws of conservation of energy and momentum, an energy of $h\nu$ and a momentum $h\nu/c$ being ascribed to each light-quantum. In contrast to this picture, the scattering of the radiation by the electrons is, on our view, considered as a continuous phenomenon to which each of the illuminated electrons contributes through the emission of coherent secondary wavelets. Thereby the incident virtual radiation gives rise to a reaction from each electron, similar to that to be expected on the classical theory from an electron moving with a velocity coinciding with that of the above-mentioned imaginary source and performing forced oscillations under the influence of the radiation field. That in this case the virtual oscillator moves with a velocity different from that of the illuminated electrons themselves is certainly a feature strikingly unfamiliar to the classical conceptions. In view of the fundamental departures from the classical space-time description, involved in the very idea of virtual oscillators, it seems at the present state of science hardly justifiable to reject a formal interpretation as that under consideration as inadequate. On the contrary, such an interpretation seems unavoidable in order to account for the effects observed, the description of which involves the wave-concept of radiation in an essential way. At the same time, however, we shall assume, just as in Compton's theory, that the illuminated electron possesses a certain probability of taking up in unit time a finite amount of momentum in any given direction. By this effect, which in the quantum theory takes the place of the continuous transfer of momentum to the electrons which on the classical

theory would accompany a scattering of radiation of the type described, a statistical conservation of momentum is secured in a way quite analogous to the statistical conservation of energy in the phenomena of absorption of light discussed above. In fact, the laws of probability for the exchange of momentum by interaction of free electrons and radiation derived by Pauli are essentially analogous to the laws governing transition processes between well-defined states of an atomic system. Especially the considerations of Einstein and Ehrenfest, referred to in § 1, are suited to bring out this analogy.

A problem similar to that of the scattering of light by free electrons is presented by the scattering of light by an atom, even in the case where the frequency of the radiation is not large enough to induce transitions by which an electron is wholly removed from the atom. In fact, in order to secure statistical conservation of momentum, we must, as emphasized by various authors*, assume the occurrence of transition processes by which the momentum of the scattering atom changes by finite amounts without, however, the relative motion of the particles of the atom being changed, as in transition processes of the usual type considered in the spectral theory. It will also be seen, on our picture, that transition processes of the type mentioned will be closely connected with the scattering phenomena, in a way analogous with the connexion of the spectral phenomena with the transition processes by which the internal motion of the atom undergoes a change. Due to the large mass of the atomic nucleus the velocity change which the atom undergoes by these transitions is so small, that it will not have a perceptible effect on the energy of the atom and the frequency of the scattered radiation. Nevertheless, it is of principal importance that the transference of momentum is a discontinuous process, while the scattering itself is an essentially continuous phenomenon, in which all the illuminated atoms take part, independent of the intensity of the incident light. The discontinuous changes in momentum of the atoms, however, are the cause of the observable reactions on the atoms described as radiation pressure. This view fulfils clearly the conditions for thermal equilibrium between a (virtual) radiation field and a reflecting surface, derived by Einstein† and considered as an argument for the light-quantum theory. At the same time it needs hardly be

* W. Pauli, *loc. cit.*; A. Smekal, *Naturwissenschaften*, xi. p. 875 (1923).

† A. Einstein, *Phys. Zeitschr.* x. p. 817 (1909).

emphasized that it is also consistent with the apparent continuity exhibited by actual observations on radiation pressure. In fact, if we consider a solid, a change of $h\nu/c$ in its total momentum will be totally imperceptible, and for visible light even vanishingly small compared with the irregular changes of this momentum of a body in thermal equilibrium with the surroundings. In the discussion of the actual experiments it may, however, be noted at the same time, that the frequency of the occurrence of such processes may often be so large that the problem arises whether the time involved in the transitions themselves can be neglected, or, in other words, whether the limit has been reached inside which the formulation of the principles of the quantum theory can be maintained (compare P. Q. T., Ch. II., § 5).

The last considerations may illustrate how our picture of optical phenomena offers a natural connexion with the ordinary continuous description of macroscopic phenomena for the interpretation of which Maxwell's theory has shown itself so wonderfully adapted. The advantage in this respect of the present formulation of the principles of the quantum theory over the usual representation of this theory will perhaps be still more clearly illustrated if we consider the phenomenon of emission of electromagnetic waves, say from an antenna as used in wireless telegraphy. In this case no adequate description of the phenomenon is offered on the picture of emission of radiation during separate successive transition processes between imaginary stationary states of the antenna. In fact, when the smallness of the energy changes by the transitions, and the magnitude of the energy radiation from the antenna per unit time, are taken into account, it will be seen that the duration of the individual transition processes can only be an exceedingly small fraction of the period of oscillation of the electricity in the antenna, so that there would be no justification in describing the result of one of these processes as the emission of a train of waves of this period. On the present view, however, we will describe the action of the oscillation of the electricity in the antenna as producing a (virtual) radiation field which through probability laws again induces changes in the motion of the electrons which may be regarded as continuous. In fact, even if a distinction between different energy steps $h\nu$ could be kept upright, the size of these steps would be quite negligible compared with the energy associated with the antenna. It will in this connexion be observed that the

emphasizing of the "virtual" character of the radiation field, which at the present state of science seems so essential for an adequate description of atomic phenomena, automatically loses its importance in a limiting case like that just considered, where the field, as regards its observable interaction with matter, is endowed with all the attributes of an electromagnetic field in classical electrodynamics.

Institute for Theoretical Physics, Copenhagen,
January 1924.

LXXVII. *The Effect of an Electric Current on the Motion of Mercury Globules in Dilute Sulphuric Acid, and its Bearing on the Problem of the Electrolytic Double Layer.* By J. E. P. WAGSTAFF, M.A., Fellow of St. John's College, Cambridge, Lecturer in Physics at the University of Leeds*.

Introduction.

IT was pointed out to me in 1920 by Professor R. Whiddington that when small globules of mercury are injected into a tube of sulphuric acid, inclined at a small angle to the horizontal, the globules can be made to move up the tube against gravity on sending a current in a particular direction through the acid. During the last two years I have made a detailed study of the motion of these mercury globules, and the results obtained and the conclusions reached to date seem of sufficient importance and general interest to justify their publication.

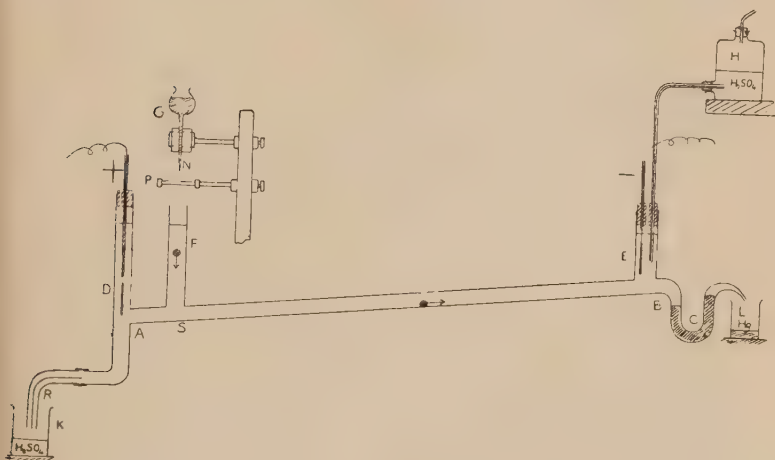
Apparatus and Method.

The tube AB (fig. 1) used for these experiments has an overall length of 50 cm. approximately and an internal diameter 0.35 cm. It is fitted with three side tubes D, E, and F of approximately the same diameter. The tubes D and E are supplied with electrodes of stiff platinum foil, which are brought into communication with the external circuit by sealing them into thin glass tubes containing mercury. The drops are formed at the end of a fine capillary tube N in hydrostatic communication with a reservoir G, the level of the mercury in which is kept constant, and they enter the apparatus through the tube F. As determinations of the masses of the mercury drops have to be made from time to time, it is convenient to have a metal ring at P for

* Communicated by the Author.

supporting the dish used to collect the drops. The U-piece C, which is initially filled with mercury, serves as a receptacle for the globules at the end of their course. At the beginning of each experiment, the mercury ejected into the beaker L is emptied back into G and used over again. In order to obtain consistent readings, it has been found necessary during the experiments to renew the acid continuously. This is best arranged by allowing a very slow stream of acid (1 drop per sec.) to enter at E and leave at R, the rates of inflow and outflow being carefully regulated until the level of the liquid in the tube shows no variation with time.

Fig. 1.



The apparatus is mounted on a substantial wooden board, which can turn about a horizontal axis so as to tilt the tube to any desired extent. When a current is passed through the acid from D to E, the globules are observed to rise up the tube and fall into B; with a current in the opposite direction the drops move down the tube. The general characteristics of the motion may be summarized thus:—

The velocity of a drop remains constant during its progress from S to B, and can thus be measured by the time taken to move over a given length of the tube. For a given potential difference between D and E, the velocity varies with the radius of the drop in accordance with the Stokes-Ladenburg law of viscosity.

Moreover, the velocity is a linear function of the potential difference between the ends of the tube. In confirmation of

this, it is interesting to notice that the globules show no tendency to travel up the tube under the action of an alternating current.

When the electrolyte is replaced by a non-conducting liquid, the motion of a mercury drop under gravity is unaffected by a potential difference applied between D and E. Mechanical forces, such as arise when a conducting sphere is placed in an electrostatic field, can therefore be neglected in any theoretical considerations of this phenomenon.

In a preliminary set of observations, three determinations of the variation of velocity with potential difference have been made for two different tubes. Each velocity quoted in the following short table is the mean of twelve observations.

TABLE I.

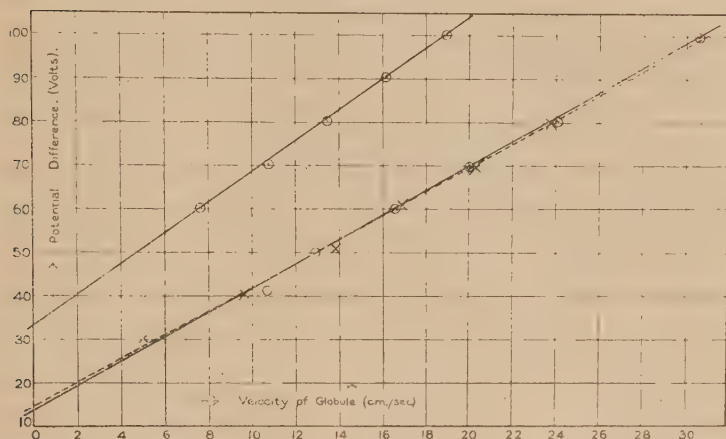
Distance l between electrodes. cm.	Inclination θ of tube to horizontal.	Radius of drop. cm.	Potential difference V between electrodes. Volts.	Velocity v of drop. cm./sec.	$\bar{V}/l \sin \theta$.
47	$\sin^{-1} \cdot 0266$	$\cdot 08786$	41	10.75	11.2
			50	12.97	
			60	16.65	
			70	20.04	
			80	24.0	
			100	30.6	
47	$\sin^{-1} \cdot 02291$	$\cdot 1208$	30	5.12	12.5
			40	9.56	
			51	13.91	
			61	16.9	
			69.5	20.26	
			80	23.72	
69	$\sin^{-1} \cdot 04534$	$\cdot 0691$	100.5	27.23	10.4
			60	7.64	
			70	10.76	
			80	13.5	
			90	16.16	
			100	18.95	

The numbers given in columns 4 and 5 indicate a linear relationship between V and v (see fig. 2). If \bar{V} is the value of V corresponding to $v=0$ (extrapolated from the appropriate curve), the values of the quantity $\bar{V}/l \sin \theta$ are approximately constant for the three experiments (column 6, Table I.)

In order to study in greater detail the effect of the size of globule, a more comprehensive set of observations is now

undertaken, the tilt θ of the tube being maintained constant throughout the series. The applied potential difference is

Fig. 2.



varied from 20 to 50 volts in steps of 5 volts. The results are given below (Table II.).

In fig. 3 the numbers given in columns 2 and 3 are plotted and, as before, v is seen to be a linear function of V . The slope of the line increases uniformly as the size of the drop diminishes. Also the lines have a common point of intersection at $v=0$, $V=15.5$ volts. At this voltage, the force in the direction SB exactly balances the resolved part of the weight for any size of drop. For voltages greater than this, drops of all sizes are urged upwards; for smaller voltages the drops move downwards.

Theory.

According to the theory of Nernst*, when a metal comes into contact with a solution, a transference of ions takes place in accordance with the respective osmotic and solution pressures. If the circuit is not completed, this transference of ions will produce a P.D. at the contact of the metal and solution, which will increase as the transference of ions continues until a limit is reached at which further transference is prevented. In the case of a mercury drop in contact with sulphuric acid, the mercury ions in solution pass to the drop since the solution pressure of the mercury is extremely small

* Nernst, *Zeitschr. Phys. Chem.* iv. p. 129 (1889).

TABLE II.

Sulphuric Acid N/10.

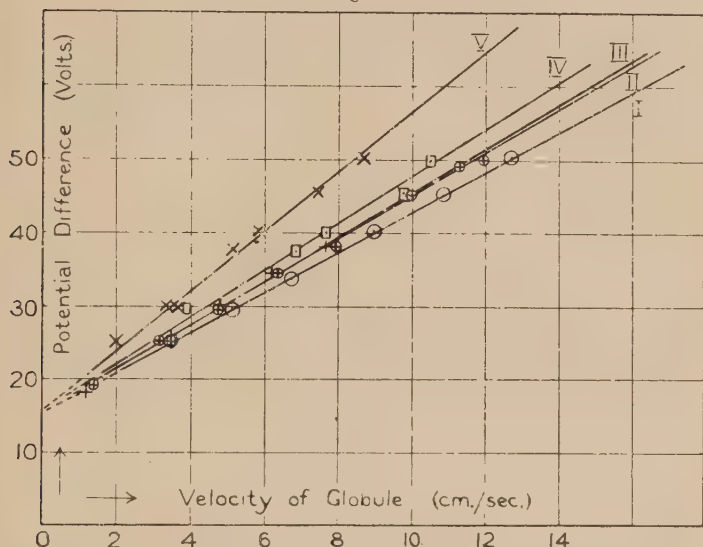
Distance l between electrodes = 47 cm.Inclination θ of tube to horizontal = $\sin^{-1} \cdot 02173$.

Radius a of drop. cm.	Potential difference V between electrodes. Volts.	Velocity v of drop. cm./sec.
·1072	20	→
	25	3·506
	29·5	5·117
	33·5	6·74
	40	8·91
	45·5	10·85
	50	12·69
·09189	19	1·430
	25	3·16
	29·5	4·74
	34·5	6·35
	38	7·95
	45	9·97
	49	11·29
·09055	25 (Repeat)	3·16
	18	1·15
	25	3·48
	29·5	4·80
	34·5	6·19
	38	7·63
	44·5	9·76
·08722	50	11·95
	20	→
	25	3·042
	29·5	3·86
	37·5	6·861
	40	7·67
	45·5	9·78
·06662	50	10·52
	25 (Repeat)	3·042
	19	→
	25	2·021
	29·5	3·63
	37·5	5·18
	40	5·87
	45·5	7·445
	50	8·694
	29·5 (Repeat)	3·415

→ indicates a distinct upward tendency difficult to measure.

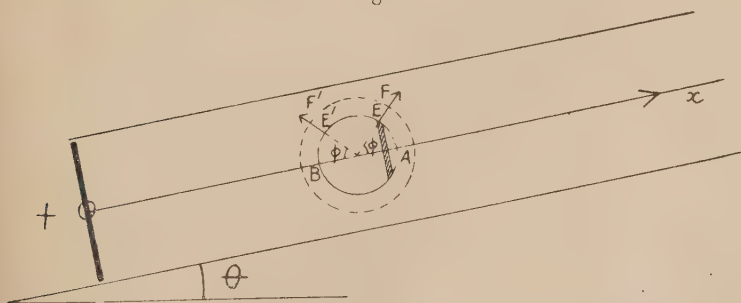
and is less than the osmotic pressure for even a very dilute solution. The mercury thus becomes positively charged, and

Fig. 3.



the whole of the charge so accumulated is derived from ions originally in solution. This positively-charged conductor repels positive ions and attracts an outer shell of negative ions to form what is to all intents and purposes a small spherical condenser of molecular thickness, the difference in

Fig. 4.



potential between the plates of which constitutes the contact potential difference V_0 . Let AB (fig. 4) represent a spherical drop of mercury of radius a surrounded by a concentric outer shell (radius $a+d$) of negative ions. d is thus the

808 Mr. Wagstaff: *Effect of an Electric Current on the*
thickness of the double layer. Let $\frac{\partial V}{\partial x}$ represent the gradient
of the externally applied potential, x being measured from
the positive electrode. If the gradient is uniform, $\frac{\partial V}{\partial x} = V/l$,
where V is the P.D. between the electrodes distance l apart.

The mechanical force per unit area of a charged conductor
is $2\pi\sigma^2$ along the direction of the normal, where σ is the
density of the charge.

The difference of potential between E and F (fig. 4)

$$= V_0 + \frac{\partial V}{\partial x} d \cos \phi = Q/C = 4\pi\sigma_E \cdot d,$$

where σ_E is the density of charge at E, and $C = a^2/d$. The
mechanical force, resolved along Ox , on a sector of the
sphere making an angle ϕ with the axis Ox is given by

$$F_1 = \left(V_0 + \frac{\partial V}{\partial x} d \cos \phi \right)^2 2\pi a^2 \sin \phi \cos \phi d\phi / 8\pi d^2.$$

Similarly, for the symmetrically situated points E', F',

$$4\pi\sigma_{E'} d = V_0 - \frac{\partial V}{\partial x} \cdot d \cos \phi,$$

and the force F_2 on the corresponding sector resolved along
 Ox is given by

$$F_2 = - \left(V_0 - \frac{\partial V}{\partial x} d \cos \phi \right)^2 2\pi a^2 \sin \phi \cos \phi d\phi / 8\pi d^2.$$

$$F_1 + F_2 = \frac{a^2 V_0}{d} \cdot \frac{\partial V}{\partial x} \sin \phi \cos^2 \phi d\phi,$$

and the total force on the sphere in the direction Ox due to
the charge on its surface

$$\begin{aligned} &= \frac{a^2 V_0}{d} \cdot \frac{\partial V}{\partial x} \int_0^{\pi/2} \sin \phi \cos^2 \phi d\phi, \\ &= \frac{a^2 V_0}{3d} \cdot \frac{\partial V}{\partial x}, \end{aligned}$$

where V_0 and V are expressed in E.S.U. If V_0 and V are
given in volts, the total force becomes

$$\frac{a^2 V_0}{3d \times 9 \times 10^4} \times \frac{\partial V}{\partial x}.$$

The resultant force along Ox acting on the sphere is

$$\frac{a^2 V_0 \frac{\partial V}{\partial x}}{3dl \times 9 \times 10^4} - \frac{4}{3} \pi a^3 (\rho - \lambda) g \sin \theta,$$

and for steady motion this is a measure of the force of viscosity which, for small velocities, can be written proportional to v .

Therefore

$$\frac{a^2 V_0 V}{3dl \times 9 \times 10^4} - \frac{4}{3} \pi a^3 (\rho - \lambda) g \sin \theta = \kappa v. \quad (1)$$

When $V = 15.5$ volts, $v = 0$;

therefore

$$\frac{a^2 V_0 15.5}{3dl \times 9 \times 10^4} = \frac{4}{3} \pi a^3 (\rho - \lambda) g \sin \theta. \quad (2)$$

Substituting in (1),

$$V - 15.5 = \frac{46.5 \kappa v}{4 \pi a^3 (\rho - \lambda) g \sin \theta} = v \tan \psi, \quad (3)$$

where ψ is the slope of the appropriate line in fig. 3. The quantity κ is not in this case numerically equal to $6\pi\mu a \times (1 + 2.4a/R)$, where μ is the coefficient of viscosity of the acid and R the inner radius of the tube, since the drop is not moving along the axis of the tube but in close proximity with the boundary, and also the motion may include rotation as well as a simple translation. Equation (3) clearly demonstrates a linear relationship between v and V , and also indicates that $\tan \psi$ increases as a diminishes.

Returning to equation (2), which expresses the condition for equilibrium of the drop, d can be calculated for given values of a , l , and θ .

In fact,

$$d = V_0 \frac{\partial V}{\partial x} \left\{ \frac{1}{4} \pi a (\rho - \lambda) g \sin \theta \times 9 \times 10^4 = \underline{1.01 \times 10^{-8} \text{ cm.}}, \right.$$

when

$a = .1072 \text{ cm.}$, $\frac{\partial V}{\partial x} = 15.5/47 \text{ volts per cm.}$, $\sin \theta = .02173$, and V_0 (the contact difference of potential) is 1 volt (see Table II.).

The theory thus gives a value for d of molecular dimensions which can be taken as confirmatory of the validity of the argument presented.

Again, since for equilibrium $\frac{\partial V}{\partial x}$ is independent of a (see fig. 3), ad/V_0 is independent of a and equal numerically to 1.089×10^{-9} on substitution in equation (2).

If E is the electrostatic charge on either plate of the small spherical condenser previously defined,

$$E = CV_0 = a^2 V_0 / d = a^2 V_0 / d \times 3 \times 10^2,$$

where V_0 is in volts.

$$\begin{aligned} \text{Therefore} \quad E &= a^3 10^7 / 3.267 \text{ E.S.U.}, \\ &= a^3 e 10^{17} / 15.58, \quad . \quad . \quad . \quad . \quad . \quad (4) \end{aligned}$$

where e is the electronic charge. The experiments indicate, therefore, that the charge on the drop is directly proportional to the cube of the radius, and for a drop of known size the magnitude of the charge can be calculated. If N is the number of mercury atoms in a surface layer of atomic thickness for a drop of radius a ,

$$N = 4\pi a^2 / (\Delta V)^{2/3} = 1.49 \times 10^{16} a^2,$$

(ΔV) being the volume of a mercury atom.

$$\text{Therefore} \quad E/N = ae/2.321,$$

and for a drop of radius .1072 cm.,

$$E/N = e/21.65,$$

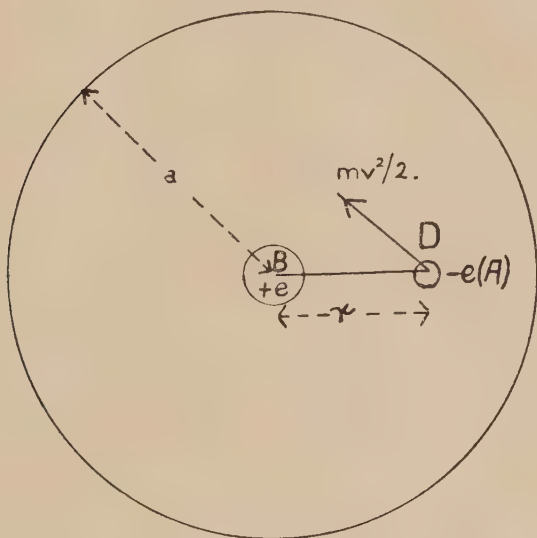
i. e. the equilibrium state requires one mercury ion in the outermost layer to 22 atoms of the mercury surface.

These experimental facts receive theoretical verification as follows:—

Consider a solution containing positively- and negatively-charged ions and neutral molecules. Let B (fig. 5) at any point of the solution be a positively-charged ion of mass large compared with the other ions when it can be regarded as fixed. We wish to find the condition that a negative ion A shall recombine with B, *i. e.* shall describe a closed orbit round B. It will be assumed that the process of recombination is not due to the direct collision between ions, but rather to collisions between ions and neutral molecules. If such a collision between A and a neutral molecule occurs at D ($BD=r$), the condition that the subsequent motion of A shall be confined to closed orbits round B is that the energy ($mv^2/2$) possessed by A after the collision is less than the work required to remove A to an infinite distance. It

will be assumed that at each collision of A with a neutral molecule the previous history is wiped out, and the ion starts out with an amount of energy appropriate at the

Fig. 5.



temperature θ . Thus A will describe a closed orbit round B if

$$mv^2/2 = 3k\theta/2 \leq e^2/r,$$

i. e.

$$r \leq e^2/\frac{3}{2}k\theta.$$

Thus, if an ion collides with a neutral molecule within a sphere of radius $r = e^2/\frac{3}{2}k\theta$, the ion is retained by B. If an imaginary sphere of radius a is drawn surrounding B, and r is written equal to βa , then

$$\beta = \frac{e^2}{a} / \frac{3}{2}k\theta = w/\frac{3}{2}k\theta.$$

The negative charge associated with the assemblage of ions in the sphere of radius r captured by B is given by $\frac{4}{3}\pi r^3(-ne)$, where n is the concentration of the negative ions per unit volume. This charge must be identical with $-e$, as the charge $+e$ is only able to reunite with one ion bearing the same charge.

$$\begin{aligned}\text{Therefore} \quad e &= 4\pi r^3 ne/3, \\ &= \frac{4}{3}\pi a^3 ne \left(\frac{w}{3/2k\theta} \right)^3,\end{aligned}$$

where $w = e^2/a$.

$$\text{Put} \quad E = 4\pi a^3 ne/3, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\text{then} \quad e = E(w/3/2k\theta)^3. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

E is the quantity of positive charge associated with the positive ions contained within a small spherical drop of the solution of radius a (fig. 5), and these are in pressure equilibrium with the surrounding liquid. If, now, the solution within the sphere a is removed, and a drop of mercury of the same radius is substituted, a charge E symmetrically distributed over the mercury surface will produce the same electrical effects in the external solution, and therefore will prevent the free passage of mercury ions from the solution to the drop. E is thus the charge on the mercury surface when equilibrium is established, and it will be noticed from (5) that E is proportional to a^3 as predicted from the experimental data.

Further, write $E = a^2 V_0/d$, where V_0 is expressed in E.S.U.; then

$$a^2 V_0/d = (\frac{3}{2}k\theta)^3 a^3/e^5, \quad . \quad . \quad . \quad . \quad (7)$$

so that the constancy of the quantity ad/V_0 follows at once from this point of view. Moreover, since it has been found experimentally that

$$V_0(\text{volts})/ad = 10^9/1.089,$$

equation (7) gives us

$$\frac{3}{2}k\theta = (e^5 \times 10^9/1.089 \times 3 \times 10^2)^{1/3}.$$

Taking $e = 4.8 \times 10^{-10}$ E.S.U., and $\theta = 289^\circ \text{ A}$,

$$k = 1.0 \times 10^{-16} \text{ erg/degree.}$$

The agreement with the accepted value of k (1.3×10^{-16} erg/degree) is therefore excellent.

The charge

$$E = (\frac{3}{2}k\theta)^3 a^3/e^5 = a^3 \times 10^7/3.126$$

on substituting for k and e , and is seen to be in close agreement with the value quoted in (4).

Equation (5) gives for the concentration of the mercury

ions in solution, $n = 1.53 \times 10^{15}/\text{c.c.}$ at $\theta = 289^\circ \text{ A.}$ and

Volume occupied by mercury ion $= 2.2 \times 10^7$ at 289° A.
 Volume occupied by water molecule

The theory thus indicates that the mercury ions in solution constitute a very small percentage of the total number of molecules present per unit volume.

It has been assumed earlier in the discussion that the energy $mr^2/2$ of a mercury ion is a measure of the temperature,

$$mr^2/2 = 3k\theta/2.$$

Also it is clear that the charge E on the surface of a mercury drop of radius a , suspended in the solution, is stationary when no ion possessing energy $3k\theta/2$ is able to penetrate the double layer a radial distance d , so that

$$\frac{3}{2}k\theta \leq \alpha Eed/a^2$$

for equilibrium, where α is a constant. Also $E = a^2 V_0/d$, so that $V_0 = 3k\theta/2\alpha e$, or V_0 is the same for drops of all sizes. Hence, since ad/V_0 is constant, the thickness of the electrolytic layer is inversely proportional to the radius of the drop. This result must follow, since the electrostatic field of a uniformly charged spherical conductor is inversely proportional to r^2 ; a small positively-charged drop is therefore able to attract a much larger cluster of negative ions. The size of d is of course limited both as to its maximum and its minimum values by further considerations. The lower limit is fixed by the ultimate size of the negative ion, and the upper limit by the consideration that, on account of thermal agitation, large clusters are liable to be broken up, the outer layers being brushed off by the impacts of other molecules.

In conclusion, returning to equation (6) and substituting e^2/a for w , E is again proportional to a^3 .

E is large when w is small in comparison with $k\theta$. This happens when either θ is large or a is large; thus high temperature and large drops assist the formation of the electrolytic layer.

At normal temperatures, on the other hand, w is much greater than $k\theta$ for sufficiently small values of a . The formation of the electrolytic double layer thus becomes increasingly difficult as the radius of the drop is decreased. In the case of a drop of the dimensions of a mercury ion (10^{-8} cm.), for example, the "charge necessary for the formation of the double layer is given by

$$E = 6.7 \times 10^{-9}e \text{ (} e \text{ the electronic charge) ;}$$

the non-existence of an electrolytic double layer in the case of drops of atomic size is thus at once explained in terms of the atomicity of electric charge. A critical diameter can be defined, below which no double layer exists. This critical diameter is given by the equation

$$E = e = e \left/ \left(\frac{w}{\frac{3}{2}k\theta} \right)^3 \right.,$$

$$w/\frac{3}{2}k\theta = 1,$$

$$e^2/a = 3k\theta/2,$$

$$\text{or} \quad a = 40\mu\mu.$$

Thus for drops of radius less than $40\mu\mu$ the double layer is absent. Working with thin films, Rücker and Reinold* found there are never any parts of the film with a thickness anywhere between $12\mu\mu$ and something between 45 and $95\mu\mu$; films whose thicknesses are within this range are unstable. The two problems may not be unassociated.

Further experiments are in progress, and will form the subject of a subsequent paper.

University of Leeds,
Jan. 1st, 1924.

Note added Jan. 28th, 1924.

A simple explanation of the working of a capillary electrometer of the Lippmann pattern can also be given on much the same lines as the above. When a small potential difference V is applied to the electrodes of a Lippmann capillary electrometer it will be assumed, provided no electrolysis of the solution ensues, that the whole of such impressed potential difference is concentrated in a layer of molecular thickness adjoining the mercury surface. In view of the small solution pressure of mercury ions such an assumption does not seem unreasonable.

An electrolytic double layer of thickness d and potential difference $V + V_0$, V_0 being the natural contact potential difference between the mercury and the solution, is thus established in the solution. The density of charge σ on the inner shell of this layer is given by $4\pi a^2 \sigma = (V + V_0) a^2 / d$ for a tube of radius a , and the pull F_1 on the surface in the direction of the axis of the tube is

$$F_1 = 2\pi^2 a^2 \sigma^2 = a^2 (V + V_0)^2 / 8d^2.$$

* Rücker & Reinold, *Phil. Trans.* clxxvii. pt. ii. p. 627 (1886).

Similarly the density σ_1 of the negative charge on the outer shell is given by $4\pi(a+d)^2\sigma_1=(V+V_0)a^2/d$, and the pull F_2 on this surface along the axis of the tube is

$$F_2=-a^4(V+V_0)^2/8d^2(a+d)^2.$$

The net pull on the layer along the axis is

$$F_1+F_2=(V+V_0)^2a/4d.$$

Again suppose that when the system has attained the equilibrium state, the meniscus is at a distance X along the tube, the origin of coordinates being chosen at the point of intersection of the axis of the capillary with the level of the mercury in the reservoir. X is defined by the condition that for a further advance δX of the meniscus along the tube, the virtual work is zero.

$$i. e. \quad \frac{(V+V_0)^2a}{4d} \delta X - 2\pi a T_0 \cos \phi \delta X - \pi a^2 (\rho - \lambda) g X \sin \theta \delta X = 0 \quad \dots \dots (I.)$$

T_0 and ϕ being the surface tension and angle of contact for the mercury-acid surface, ρ and λ the densities of the mercury and acid respectively, and θ the inclination of the tube to the horizontal. When the externally applied potential V is zero, the value of X say \bar{X} is defined by the equation

$$\frac{V_0^2a}{4d} - 2\pi a T_0 \cos \phi = \pi a^2 (\rho - \lambda) g \bar{X} \sin \theta \quad \dots (II.)$$

This corresponds to the normal position of the mercury in the capillary. The change in position of the mercury-acid meniscus corresponding to an applied potential V is given by

$$X - \bar{X} = (\bar{V} + V_0^2 - V_0^2)/4\pi ad(\rho - \lambda)g \sin \theta,$$

which is a parabola giving a minimum value for $X - \bar{X} =$

$$-V_0^2/4\pi ad(\rho - \lambda) \sin \theta g, \quad \dots \dots (III.)$$

at $V = -V_0$. The thread of mercury thus recedes to its minimum position when the applied potential difference just neutralizes the contact potential difference. If d be evaluated from (III.) for an actual set of observations, it is of the order 10^{-8} cm. Finally, if the minimum value of $X - \bar{X}$ is independent of the radius of the capillary tube, $ad.V_0$ is constant as suggested by the experiments with the moving mercury globules.

LXXVIII. *The Adjustment of Observations.**By* NORMAN CAMPBELL, *Sc.D.***Summary.*

1. PROFESSOR EDGEWORTH has recently suggested the use of medians, as an alternative to least squares (L.S.), for reducing observations involving two variables, on account of their superior facility. Opportunity is therefore taken to press once more the claims of the method of zero sum (Z.S.), which is even simpler.

2. The method is described again with special reference to two variables.

3. Some more examples are given, including those of Prof. Edgeworth.

4. It is urged again that there is no reason to believe that Z.S. is necessarily inferior in accuracy to L.S., or

5. If it is inferior, that the difference is significant.

6. Some methods are discussed whereby it might be possible to decide experimentally whether Z.S. is inferior to L.S. Such applications of them as have been made do not indicate any difference between the two methods appreciable to experiment.

1. Prof. Edgeworth's paper on "the Use of Medians for reducing Observations" (Phil. Mag. xlv. p. 1074, 1923), encourages me to press once more the claims of the method of Zero Sum (Z.S.) which was described in Phil. Mag. xxxix. p. 177, 1920. For Prof. Edgeworth, while holding that the method of Least Squares (L.S.) is always the best of all, urges that in some cases the method of medians may be employed on account of its greater convenience. If it is once admitted that convenience may even be a factor determining the choice of method, the claims of Z.S. are overwhelming; in convenience it surpasses far all proposed arithmetical methods, and often even graphical methods. And yet, so far as I know, the method is not habitually used by anyone but myself.

2. Perhaps it is permissible to describe the method once more, confining attention this time to the form that it takes in the vast majority of physical problems, when the number of variables and of constants to be determined is 2. In such

* Communicated by the Author.

problems, measurements have been made on each of two magnitudes, x , y , which are known (or assumed) to be related by the linear equation

$$y = a + bx. \quad (1)$$

A measurement of x with its associated y constitutes a single observation. The problem is to find values of a and b which make the observations fit closely to the equation (1); it is solved by Z.S. as follows:

(1) Arrange the n observations in the order of the magnitude of that variable which is intentionally changed in passing from one observation to another. If the equation (1) is of the form given, this magnitude will usually be x , and the observations are to be arranged in ascending or descending order of x . It is usually possible to enter the observations in this order in the note-book; if this is done, the trouble of writing them out again is saved.

(2) Divide the observations centrally into two halves, the first half constituting one set, the second another. If n is odd, halve the central observation and count one half in each set.

(3) In each set add together all the x 's and all the y 's, forming the sums $\Sigma_1 x$, $\Sigma_1 y$ for the first set, and $\Sigma_2 x$, $\Sigma_2 y$ for the second.

(4) Solve for a and b the two simultaneous equations

$$\left. \begin{aligned} \Sigma_1 y &= \frac{n}{2} \cdot a + b \cdot \Sigma_1 x \\ \Sigma_2 y &= \frac{n}{2} \cdot a + b \cdot \Sigma_2 x \end{aligned} \right\} \quad (2)$$

The resulting values of a and b are those required.

(5) The arithmetic is so simple that "checks" other than repetition are seldom required. But if for any reason the residuals (*i. e.*, the difference between the observed y 's and those calculated from (1) by the use of the deduced values of a and b) have to be computed, a check can be obtained by observing that the sums of the residuals in each set must be accurately zero, except in so far as figures have been rounded off in computing.

If the observations are arranged originally in the required order, it is quicker to find a and b arithmetically than by the usual graphical process. The ease of the method can be

realized from the fact that Ex. IV. below, involving 54 observations, was worked out (apart from computing the residuals) during a train journey of 20 minutes, without the use of tables and writing on nothing but the margin of the printed page.

3. A few examples may now be given. Of these, only one is in the least typical of normal physical problems, namely Example IV. ; it is chosen because it is so typical. The other three are those of which the figures are given by Prof. Edgeworth. They are included only to show that the method works and gives at least a good approximation in the most unlikely examples. In Examples II. & III., in the absence of the necessary information, the observations, for the purpose of division into sets, have been arranged in the order in which they are printed. Prof. Edgeworth's result has been added to his own examples ; but, since the median method is not discussed here, it is omitted from Ex. IV., to which it is not easily applicable. In each example, the residuals and the sum of their squares are given for each method of reduction *.

EXAMPLE I.

Edgeworth's Ex. 1.

L.S.	$a=1.784 \pm 0.039$	$b=0.369 \pm 0.025$
Z.S.	$a=1.789$	$b=0.396$
Median	$a=1.745$	$b=0.368$

Residuals.

	L.S.	Z.S.	Median.
	+0.0347	+0.0757 *	+0.0676
	-0.0480	-0.0450	-0.0233
	-0.0479	-0.0614	-0.0277
	-0.0210	-0.0430	-0.0036
	+0.0980	+0.0737	+0.1120
Σv^2	0.0158	0.0188	0.0184

* Prof. Edgeworth's x and y correspond to my a and b , except as regards a factor common to both. The conventional notation, whereby the constants a and b are represented by x and y , symbols otherwise confined to variables, is confusing. The reason for it is, of course, that, for the purpose of the adjustment of observations, the constants are the unknowns to be determined. In Example I. 0.1669 is clearly a misprint for 1.669.

EXAMPLE II.

Edgeworth's Ex. 3.

L.S.	$a=1.019 \pm 0.332$	$b=0.0153 \pm 0.0203$
Z.S.	$a=0.776$	$b=0.0242$
Median.	$a=0.943$	$b=0.0182$

Residuals.

L.S.	Z.S.	Median.
- 9.40	- 8.93	- 9.16
- 0.33	+ 0.46	0
+13.66	+14.52	+14.14
- 6.39	- 6.04	- 6.26
-27.77	-36.95	-30.53
+27.87	+20.19	+25.56
+10.50	+ 8.98	+10.05
+10.42	+ 7.79	+ 9.63
Σv^2	2083	2208
		2102

EXAMPLE III.

Edgeworth's Ex. 5.

L.S.	$a=25533.6 \pm 16.1$	$b=244.3 \pm 32.7$
Z.S.	$a=25537.4$	$b=250.4$
Median.	$a=25406.6$	$b=483.1$

Residuals.

L.S.	Z.S.	Median.
+18.07	+ 5.19	+452.72
+80.54	+ 73.00	+155.19
-51.96	- 62.09	- 2.16
-16.28	- 32.08	+ 21.87
-28.03	-102.34	- 0.05
+51.32	+ 28.13	+ 38.31
+99.73	+ 90.29	+ 21.70
Σv^2	23144	29657
		231461

EXAMPLE IV.

Zwetsch, *Zeit. f. Phys.* xix. p. 407 (1923).

L.S.	$a=0.0131135 \pm 0.0000093$	$b=0.000000175 \pm 0.000000023$
Z.S.	$a=0.0131045$	$b=0.000000200$

Residuals $\times 10^6$.

L.S.	Z.S.	L.S.	Z.S.	L.S.	Z.S.
+36	+30	-28	-30	-02	+01
-41	-47	+01	-01	-19	-16
+16	+10	+00	-01	-12	-08
-41	-47	-50	-51	+12	+16
-11	-17	-12	-13	+36	+39
-29	-35	+09	+08	+14	+17
+13	+07	+41	+40	-16	-12
-25	-31	+36	+35	+20	+23
+10	-04	+29	+28	-21	-18
+44	+40	+04	+05	-58	-53
-05	-09	-27	-26	+42	+48
-35	-39	-12	-11	+25	+31
+66	+62	+02	+03	-01	+05
-18	-22	-44	-43	+30	+36
-01	-05	-10	-09	+20	+26
+20	+16	-19	-18	-22	-16
+48	+44	-20	-19	+29	+35
+28	+25	-24	-23	-20	-14

 Σv^2 (L.S.) 41740×10^{-12} (Z.S.) 42982×10^{-12} .

The examples confirm the results indicated by those given previously and by the numerous examples arising from my own experiments—namely, that the difference between the Z.S. and L.S. values never much exceeds the probable error of the latter, even though n is small, systematic error is suspected, and the conditions are generally unfavourable to agreement. Further, since a difference of as much as the p.e. may seem serious, it should be pointed out that this way of expressing the difference is misleading. In the Zwetsch example, which alone is typical of the method, though the difference between Z.S. and L.S. is about equal to the p.e. for both a and b , the difference in Σv^2 is less than 3 per cent., and the difference in the “corrected refraction” (which it is the object of the experiment to find) is very much less than the p.e. For this quantity L.S. gives 291.41 ± 0.39 , while Z.S. gives 291.45.

4. But though the differences between the values given by L.S. and Z.S. are small in these examples, and in all the very much greater number that I have examined, it is possible that they are significant. If, as seems still to be believed generally, L.S. is more accurate than any other

method, it may be necessary sometimes, if not always, to face the greater amount of work which it entails.

In the previous paper, and in my 'Physics,' Chs. xvi. and xvii., reasons have been given for thinking that the general belief is unfounded; and I have little to add to what has been said already and nothing to subtract from it*. But I would venture to put the position again. It is not urged that L.S. is wrong or that Z.S. is right; for I do not think that in the adjustment of observations any method can be definitely right; there is always a margin of uncertainty which, from the very nature of the case, it is impossible to abolish. What I do maintain is that there is no reason to believe that L.S. is more often right than Z.S. Again, it is not denied that L.S. is a valid logical deduction from certain premisses—though mathematicians do not seem wholly agreed from what premisses it is deducible. Given those premisses, L.S. is certainly right and Z.S. wrong. But I deny that there is any evidence that premisses from which L.S. can be deduced are true in the experimental sense.

If propositions having any bearing on experiment are to be deduced from the premisses of a theory of error, those premisses must contain experimental conceptions, or ideas capable of interpretation in terms of experimental conceptions. Such conceptions are involved in the foundations of the orthodox theory of errors in two ways. First, they are involved in the assertion that the "most probable" value is the right value to take for experimental purposes. Those who have not inquired deeply into the matter are apt to forget how very complex and difficult is this idea of "most probable." It is introduced by the fundamental theorem of inverse probability, of which Bayes's theorem is one form.

* *Note added in correction.* I criticised certain of the well-known rules for adjustment according to the Method of L.S. on the ground that, in special cases, they led to absurd results. This criticism has offended greatly Dr. R. M. Stewart (Phil. Mag. xl. p. 217, 1920) and Mr. H. S. Uhler (J. Opt. Soc. Amer. vii. p. 1043, 1923). They admit that the rules quoted are not applicable to these cases; but they maintain that it is not consistent with the principles on which the Method of L.S. is based so to apply them; they give alternative rules based on those principles. But these principles are precisely what I reject; any rules based on them are, for me, purely empirical; and I can admit no error in comparing them, as empirical rules, with the rule, equally empirical, which I propose to take their place. If I have been guilty of error, it is merely in applying the term "Method of L.S." to the rules rather than to the principles on which they are professedly founded. The only important question, namely whether the principles have any validity, these authors do not discuss; Dr. Stewart starts by assuming explicitly precisely those propositions which I am most concerned to deny.

Now, though this theorem is apparently accepted by all mathematicians who write on probability—for without it the theory of errors would not be mathematical at all,—no two of the most prominent exponents of the subject appear to agree exactly why it is true or exactly what it means. I do not propose to discuss it further here, but physicists, who are apt to accept “most probable” simply as synonymous with “most nearly right,” ought to be warned that the matter is not nearly as simple as it appears at first sight.

Experimental conceptions are introduced again in the premisses, whatever form they may take, which imply the Gaussian law of the distribution of errors. Of this law, no direct proof has been or can be offered. It is known that in many cases the distribution of the residuals is very near to the Gaussian and in no case widely different from it. But it is admitted that the residuals are not the errors; and what we actually know is always the residuals and not the errors. And it must be insisted once more that, by no possibility, can the true law be exactly Gaussian. Since all measuring instruments have a “step,” and since all observations have a least significant figure, the number of possible values within a given range is finite. The true law of distribution must be discontinuous, not continuous. That is an elementary fact which no amount of argument will alter; the Gaussian function can at best be the continuous function which fits most nearly an essentially discontinuous series of points. But it is by no means certain that it is even this. The existence of the “decimal error” in subdividing a division is well known nowadays, and its distribution is not even approximately Gaussian. Further, the more nearly the “observations” represent real direct observations, unaltered by corrections or the taking of means, the more often (in my experience) is a deviation from the Gaussian distribution to be suspected. Example IV. is typical in this respect. The following table indicates that in the neighbourhood of zero error, the chance of an error does not decrease as rapidly with increase of its magnitude as the Gaussian law would predict; this feature is extremely frequent and is not unlikely on general grounds:—

Number of residuals between	0 and 9	Actual.	Calculated.
		10	15
	10 „ 19	13	13
	20 „ 29	15	10·5
	30 „ 39	6	7
	40 „ 49	7	4·5
	50 „ 59	2	2
	60 „ 69	1	1

For all these reasons it seems to me ridiculous to pretend that L.S. is so firmly established as the one and only correct method that no other is worth serious consideration, except perhaps as a mere approximation. According to the theory of error on which L.S. is based, Z.S. must approach asymptotically to it as the number of observations is increased. When that number is comparatively small, the minor departures from the premisses on which the theory is based are likely to be most serious; it is then that the question between Z.S. and L.S. really arises, and it is then that the unique validity of L.S. is most doubtful.

5. Again, even if it is admitted that L.S. must be in general somewhat nearer to the truth than Z.S., the question still remains whether the difference between the two is significant. Unless that question can be answered affirmatively, there will be no justification for the greater labour involved in L.S. Assuming the Gaussian theory, it might be possible, though extremely difficult, to calculate by how much the error of Z.S. in general exceeds that of L.S. But the result would tell us nothing about the relative merits of the methods, unless it could be shown that, in some possible experiment, the difference could be detected. And, if there is such an experiment, there is no need for argument; the matter will be settled in a manner beyond dispute.

Accordingly, it will be well to consider what kind of experiment might give the decision desired. If it can be found, it is sure to be exceedingly complicated and laborious, for the inquiry must necessarily be statistical: the Gaussian theory does not predict that L.S. gives always the true value, or always a value nearer the truth than any other method; it predicts only that in general the result will be nearer the truth. But the labour ought not to be shirked. The immense mathematical structure of the Gaussian theory rests on a very slight experimental foundation; a few superficial inquiries into the distribution of residuals is all the experimental evidence in its favour that is usually offered. It is time to divert attention from the elaboration of the superstructure to the strengthening of the foundations.

6. A decision would be possible if a and b were already known from some source of information independent of the observations. Such a condition is impossible to fulfil completely and satisfactorily; for reduction of observations by numerical computation is justifiable only when the observations themselves are as accurate as possible; if any known and avoidable source of error is present, it will almost always include some systematic error, which will not be

completely eliminated by any method of reduction. However, an approximation to the condition can be made. Suppose, for example, that we place a battery of E.M.F. E_0 in series with resistance R , an ammeter, a rheostat, and another source of potential, and read the current i flowing in the circuit together with the P.D. E between its ends. If r_1 and r_2 are the resistances of the battery and ammeter,

$$E = E_0 + i(R + r_1 + r_2), \quad \dots \quad (3)$$

which is of the form (1), if $a = E_0$ and $b = R + r_1 + r_2$. E_0 and the resistances can be measured independently by potentiometer and bridge methods of very great accuracy. The absolute values assigned to a and b will depend on the calibrations of the voltmeter and ammeter, which are subject to errors of the same order as those of the calculated a and b ; but if E_0 , R , are changed between successive experiments, the relative values are independent of calibration; further, if they are changed by reversals of the cells composing E_0 , and by the combination in series or parallel of the resistances composing R (r_1 and r_2 being small and known approximately), no absolute measures are necessary for the comparison.

This experiment has been carried out*, 15 comparisons being made. In 5 of them, the results of L.S. and Z.S. were practically indistinguishable. Of the remaining 10 cases, Z.S. was appreciably the more correct in 6, L.S. the more correct in 4. The comparison, if it displays any difference, is in favour of Z.S. It should be noted that, as the residuals showed, the errors were mainly "decimal," and therefore not distributed according to the Gaussian law.

A comparison of the same kind might be made in experiments directed to the determination of constants which are known theoretically. Thus observations by different methods of the value of h might be reduced by the two methods. The published results are not given in so much detail that the comparison can be made; and, even if they were, the strong probability that different methods are affected by different systematic errors would make the comparison uncertain.

7. Another possible method might be based on an examination of the maximum residual. Quite apart from any theory of errors, it is often possible to estimate, from the nature of the measurement and of the instruments with

* The experiments were made in 1914; the complete records have been lost, but a summary of them was recovered recently.

which it is made, the maximum error which can occur in taking an observation. If a reliable estimate of this maximum error can be made, and if any residual is found to exceed that error, then the value from which the residual is a difference cannot be the true value; the method of adjustment leading to that value must be false.

Such a method, if it could be applied, would be unexceptionable. But I have never succeeded in making any distinction between L.S. and Z.S. by means of it. Since authors (rightly) do not usually publish enough details of their experimental methods to enable the maximum error to be ascertained by others, I have been perforce confined to my own experiments, none of which have made any pretence to the highest accuracy. I have always found that, if only those experimental errors are taken into account which arise from the measuring instruments and can therefore be definitely foreseen, the maximum residual is always greater than the maximum error, whichever method of adjustment is adopted. If, on the other hand, allowance is made (as it doubtless should be) for failures to realize exactly the conditions intended, and for mere mistakes in reading or entry, the possibilities of error are so numerous and so vague as to lead to a maximum much greater than any residual. The method is commended to those whose experiments are better adapted to the purpose; but since the difference between the maximum residuals of L.S. and Z.S. is usually small, and not always in the same direction, the prospects of a decision by this method are not bright.

8. There is a third possible method less satisfactory theoretically than either of these, but easier to apply. It is familiar to all experimenters that the accuracy of a numerical result cannot be increased indefinitely (as it could be if the simple Gaussian theory of errors were true) by increasing the number of observations; the accuracy, for the purpose of this statement, is judged by the degree to which a repetition of the experiment leads to a repetition of the result. Suppose, then, that we make a number of determinations of the same a and b , each determination consisting of a considerable number of observations, reduce them both by L.S. and Z.S., and compare the degree of consistency given by the two methods of reductions. If one method of reduction gives notably better consistency than the other, there is some presumption in its favour. Such comparisons have been made, using measurements obtained in the calibration of Pirani pressure gauges; it should be noted that here there is known to be some slight systematic error, since the relation

involved is not perfectly linear. Four series of measurements were made on each of 7 gauges, each series consisting of from 22 to 26 observations. The maximum difference between two determinations for the same gauge, reduced by the same method, expressed as a fraction of the mean probable error was, for the 7 gauges

L.S. : 0.6, 1.4, 1.7, 1.3, 1.8, 0.7, 1.5.

Z.S. : 0.6, 1.6, 1.6, 1.1, 2.0, 0.9, 1.7.

The comparison this time is slightly in favour of L.S., but can hardly be regarded as more significant than the contrary result in the first test.

Such experimental tests of the efficiency of different methods of reducing observations are exceedingly tedious, and it is improbable that I shall have the opportunity of making many more of them. Anyone who is interested in the subject can easily continue them. In the meantime I would suggest that the onus of proof lies on those who would maintain that the superior accuracy of L.S. justifies the very great additional labour which it requires. Once more, it is useless to produce elaborate mathematical arguments to prove that L.S. in general gives the more correct value; if there is any physical significance in the statement that it is more correct, there must be some experimental test which will establish the statement; the only way to establish the statement is to make that test.

LXXIX. *Relative Probabilities of the Transitions involved in the Balmer Series Lines of Hydrogen.* By FRANK C. HOYT*.

I. *Introduction.*

ACCORDING to the quantum theory, the factors of fundamental importance for the processes of emission and absorption are the probabilities of transition in unit time from one stationary state of the atom to another, as introduced by Einstein in his deduction of Planck's law of temperature radiation. The correspondence principle of Bohr offers the possibility of connecting these probabilities with the properties of the motion of the atom, and thereby a basis for the estimation of the intensity of spectral line. In a previous paper† the general theory was briefly described,

* Communicated by Prof. N. Bohr.

† F. C. Hoyt, *Phil. Mag.* xlv. p. 135 (1923).

and some calculations of the relative intensities of X-ray lines were made on the basis of various plausible assumptions as to the exact relations between these probabilities and the motion; but as yet, however, there do not exist sufficient experimental data for a sharp distinction between these assumptions in this way. In the case of optical emission spectra, the number of atoms present in the initial states of the transitions involved in the emission of different lines is a factor which is very uncertain under the ordinary methods of excitation. This difficulty was avoided in the case of X-ray spectra, where the initial state is the same for a number of lines; but here the problem is greatly complicated by the complexity of the electronic motions. In optical absorption spectra we have to do, in many cases, with transitions from the same initial state of the atom, and it will be of particular interest to consider the lines of the Balmer series of hydrogen in this connexion, because here the motion may be completely treated on the basis of ordinary mechanics. To obtain direct absorption data of the necessary kind for these lines will perhaps present great difficulties; but, as pointed out by Ladenburg*, it may be possible to establish a connexion between the relative dispersion effects of spectral lines and the quantities which determine their relative absorption. In fact, Ladenburg and Reiche† have been able to obtain in this way an estimate, from dispersion data, of the relative probabilities of spontaneous transitions for H_α and H_β , which are in general agreement with the values indicated by a qualitative estimate based on the correspondence principle. It may therefore be of interest to make a comparison of the dispersion data with the values of these probabilities estimated on the various assumptions as to the quantitative application of the correspondence principle discussed in the previous paper.

II. *Calculation of the Probabilities of Transition for the Components of the Balmer Lines of Hydrogen.*

On the correspondence principle the probabilities of transition may be estimated by a comparison of the rate of emission of energy by a classical harmonic oscillator of frequency ν and amplitude Q with the quantity $h\nu A'_{nn}$, which represents this rate of emission on the quantum theory.

* R. Ladenburg, *Zeits. für Phys.* iv. p. 451 (1921).

† Ladenburg & Reiche, *Naturwissenschaften*, ix. p. 584 (1923).

This leads at once to the relation

$$A'_{r''} = \frac{1}{\hbar\nu} \frac{32\pi^4 e^2}{3c^3} Q^2 \nu^4, \quad . \quad . \quad . \quad . \quad (1)$$

where $A'_{r''}$ is the probability of spontaneous transition in unit time, and $Q^2 \nu^4$ may be considered as a kind of mean value of $C^2 \omega^4$, where ω and C are the frequency and amplitude of the corresponding harmonic component. For a multiply periodic system of degree of periodicity u , the frequency of the radiation emitted by a transition between two stationary states for which

$$\begin{aligned} I_r &= n_r' h \\ I_r &= n_r'' h \end{aligned} \quad (r=1, \dots, u)$$

respectively will, in fact, as pointed out by Kramers, be given by the formula

$$\nu = \int_0^1 \omega_\lambda d\lambda,$$

where λ is an auxiliary variable defining an intermediate state by the relation

$$I_r = I_r'' + \lambda(I_r' - I_r'').$$

The following six methods of evaluating the mean value were briefly discussed in the previous paper :—

$$Q^2 = \int_0^1 C_\lambda^2 d\lambda, \quad (A)$$

$$Q = \int_0^1 C_\lambda d\lambda, \quad (B)$$

$$\log Q = \int_0^1 \log C_\lambda d\lambda, \quad (C)$$

$$Q^2 \nu^4 = \int_0^1 C_\lambda^2 \omega_\lambda^4 d\lambda, \quad (D)$$

$$Q \nu^2 = \int_0^1 C_\lambda \omega_\lambda^2 d\lambda, \quad (E)$$

$$\log (Q \nu^2) = \int_0^1 \log (C_\lambda \omega_\lambda^2) d\lambda. \quad (F)$$

In the case of the hydrogen atom these quantities may be evaluated by graphical integration from the well-known expression for the harmonic representation of a rotating

ellipse, and in Table I. are given the relative values of A'' for the fine-structure components of H_α and H_β , the two first lines of the Balmer series, the letters at the head of the columns corresponding to the six methods of averaging

TABLE I.
Relative Values of A'' .

Transition.	A.	B.	C.	D.	E.	F.
$\alpha_1 \ 3_3-2_2$	1	1	1	1	1	1
$\alpha_2 \ 3_2-2_1$	·451	·444	·432	·397	·414	·434
$\alpha_3 \ 3_1-2_2$	·0188	·0135	·00410	·00547	·00605	·000475
$\beta_1 \ 4_3-2_2$	·371	·316	·2371	·182	·169	·104
$\beta_2 \ 4_2-2_1$	·325	·303	·275	·354	·260	·172
$\beta_3 \ 4_1-2_2$	·0258	·0144	·00346	·00240	·00270	·00130

given above. From these values and the theoretical values of the statistical weights in the stationary states the probability coefficients B'_i and B''_i for the forced transitions may be readily found from Einstein's relations,

$$B'_i = \frac{g'}{g''} A'_i \frac{c^3}{8\pi h \nu^3},$$

$$g'' B'_i = g' B''_i.$$

Here g' and g'' are respectively the statistical weights of the stationary state of higher and lower energy. These weights are in the present case proportional to the subordinate quantum integers.

III. Discussion of the Calculations.

Unfortunately there exists at present no fully adequate basis for a comparison of these calculated probabilities with experiment. From measurements on the absorption of the Balmer lines such a comparison might, however, be made in the following way. If N'' is the average number of atoms per unit volume present in the state of lower energy, the rate of absorption of energy is given by the expression

$$\rho_\nu N'' B''_i h \nu,$$

where ρ_ν is the density of radiation of frequency ν . We

thus have for the average coefficient of absorption σ for a given line

$$\sigma = N'' B_i h\nu,$$

or, making use of Einstein's relation,

$$\sigma = N'' \frac{g'}{g''} A'' \frac{c^3}{8\pi\nu^2}.$$

In Table II. are given the relative values of σ for the fine-structure components of H_α and H_β computed from eq. (2) and from the values of A'' in Table I. Now, in any ordinary experiment the components would hardly be separated, and it will be necessary to estimate the total absorption of the

TABLE II.

Relative Values of $\sigma/N'' = \frac{g'}{g''} A'' \frac{c^3}{8\pi\nu^2}$.

Transition.	A.	B.	C.	D.	E.	F.
$\alpha_1 \ 3_3-2_2$	1	1	1	1	1	1
$\alpha_2 \ 3_2-2_1$	·600	·592	·576	·529	·552	·579
$\alpha_3 \ 3_1-2_2$	·00627	·00449	·00137	·00182	·00202	·000158
$\beta_1 \ 4_3-2_2$	·151	·129	·0963	·0741	·0686	·0421
$\beta_2 \ 4_2-2_1$	·176	·164	·149	·192	·141	·0934
$\beta_3 \ 4_1-2_2$	·00350	·00195	·000469	·000325	·000364	·000176
$\sigma_\alpha = \frac{2a_1 + a_2 + 2a_3}{2\beta_1 + \beta_2 + 2\beta_3}$	5·39	6·12	7·53	7·44	9·17	14·5

three components of each line. Here we must take into account the relative number of atoms present in the different initial states. Under conditions of thermal equilibrium we should have

$$N'' = \text{const.} \times g'' e^{-\epsilon''/kT},$$

where ϵ'' is the energy and T the temperature. At sufficiently high temperatures the values of N'' would thus be proportional to g'' since the differences in energy are small, and there would be twice as many atoms in the 2_2 states as in the 2_1 states, the statistical weights, as above mentioned, being in this case proportional to the subordinate quantum integers. The values of the ratio $\sigma_\alpha/\sigma_\beta$ given in the last row

are calculated on this assumption. It may, however, be emphasized that if the excitation is not produced by thermal equilibrium but, for instance, by electron bombardment, the ratio of the number of atoms in the 2_1 and 2_2 states may be very different from that used in the calculation.

The relative values of σ could be found from measurements of the total absorption and compared with the values calculated by eq. (2), but such data do not exist for these hydrogen lines, and to obtain them might involve very great difficulties. However, as suggested by Ladenburg, the relative values of σ may be obtainable from measurements on anomalous dispersion. In fact, according to the classical theory as ordinarily interpreted, the quantity σ is given by the expression $N \frac{\pi e^2}{m}$, and the same expression

occurs in the classical dispersion formula. Ladenburg has therefore, in the paper mentioned in the Introduction, taken the view that the probabilities of transitions between stationary states, which on the quantum theory are responsible for the absorption, may be obtained from the course of the dispersion curve in the neighbourhood of the absorption line. In this way he has, from his measurements on the dispersion of H_α and H_β in luminous hydrogen, arrived at the value 4.5 for the relative absorption coefficient $\sigma_\alpha/\sigma_\beta$ as a mean of values lying between 3 and 6.

The results in this table are seen to differ greatly for the different methods of averaging used, and dispersion data might therefore be of importance for an eventual choice between these methods. At present, however, the experimental data are hardly of sufficient accuracy to allow a definite choice. In this connexion it may be remembered that the experiments among other uncertainties involve a fundamental one on account of the fact that the measurements of the dispersion are made under a heavy electric discharge. As pointed out by Ladenburg, this discharge may have a considerable influence on the structure of the lines due to the perturbations of the electronic orbits. It may also considerably affect the ratio between the number of atoms present in the initial states.

The author wishes to express his thanks to Professor N. Bohr for his kind interest in the preparation of his paper.

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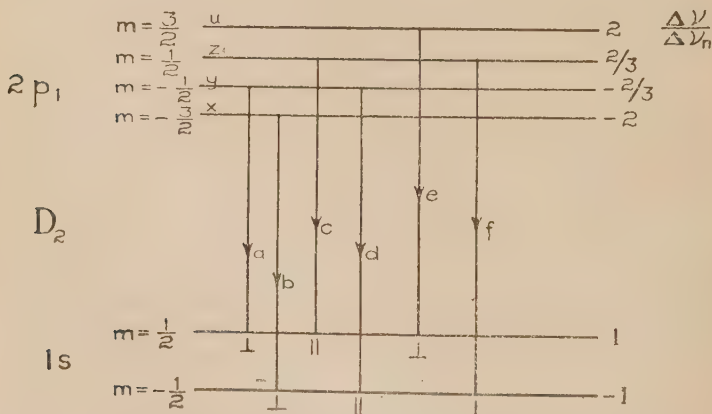
LXXX. *The Polarization of Resonance Radiation.* By G. BREIT, *National Research Fellow, The University of Minnesota* *.

EXPERIMENTS on the polarization of resonance radiation in a magnetic field have been described by Wood and Ellett †, and the Zeeman effect in resonance radiation has been discussed theoretically by Foote, Ruark, and Mohler ‡. I should like to point out that the Zeeman effect discussed in accordance with the Landé-Sommerfeld-Heisenberg theory in the manner of Foote, Ruark, and Mohler accounts for the magnitude of polarization observed in sodium vapour, and to accentuate the difference in the observed behaviour of sodium and mercury in an external field.

1. Polarization in Strong Fields.

We first discuss the effects in a magnetic field of sufficient strength (100 gauss) to make the state of polarization depend mainly on the field. Sodium will be used as an example, since the data are more complete for this element. The

Fig. 1.



Zeeman patterns of D_2 and D_1 are due to transitions between levels drawn in figs. 1 and 2. The arrows indicate transitions and the signs \parallel or \perp indicate that the component is polarized parallel or perpendicular to the applied field. We take D_2

* Communicated by the Author.

† Proc. Roy. Soc. A, ciii. p. 396 (1923).

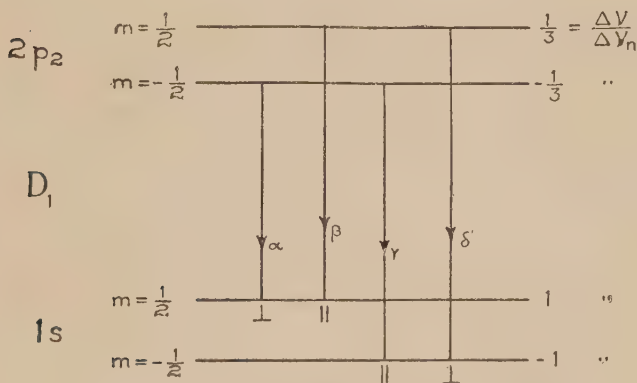
‡ Journal of the Optical Society of America, vii. p. 415 (1923).

to be twice as strong as D_1 and the relative intensities of the Zeeman components to be as given by Paschen and Götze in *Seriengesetze der Linienspektren* (Berlin: Julius Springer, 1922), p. 154, so that

$$\frac{a}{8.8} = \frac{b}{14.6} = \frac{c}{14.6} = \frac{\alpha}{10} = \frac{\beta}{9} \dots \dots \dots (I)$$

If the intensities of the Zeeman components had been measured in a tube-furnace with a small outlet, the statistical populations of all the $2p_1$ levels would be the same to a good approximation. The same is true for the levels of $2p_2$. The numbers given in (1) will measure, therefore, actual probabilities of transitions.

Fig. 2.



To obtain the relative intensities of the Zeeman components in resonance radiation, we need some conceptions introduced by Einstein* in his derivation of Planck's radiation formula. Let E_m and E_n be the energies of a gas molecule in two quantized states m and n respectively. Let m be greater than n . If the molecule is in the state m , there is a probability $A_m^n dt$ that in the time dt it will pass spontaneously to n with emission of radiation. A_m^n is a constant for a given combination of indices.

If the molecule is surrounded by radiation passing in random directions the volume density of which is $\rho(\nu)d\nu$ for the frequency range $\nu, \nu + d\nu$, the probability, due to ρ , of a change of state from n to m per second is written by Einstein as $B_n^m \rho$, and the probability of a change from m to n is similarly written as $B_m^n \rho$. If the *a priori* probabilities of n and m are

* *Phys. Zeit.* xviii. p. 121 (1917).

p_n, p_m respectively, Einstein showed that

$$p_n B_n^m = p_m B_m^n,$$

and that

$$\frac{A_m^n}{B_m^n} = \alpha \nu^3,$$

where α is a universal constant.

Therefore if $\frac{p_n}{p_m}$ is kept constant, $\frac{A_m^n}{B_m^n}$ is also unchanged.

This fact is fundamental in the derivation below.

Under the experimental conditions used by Wood and Ellett the pressure is so low that the excitations of D_1 and D_2 are separate *, and the incident radiation is so weak that the amount of resonance radiation is proportional to the incident energy.

The above considerations apply to black-body radiations reacting with an atom of the simplest type, and do not take into account the influence of polarization. A slight modification of the above concepts must be made if polarization is considered.

In a magnetic field the emission occurs in quanta, some of which are linearly and some circularly polarized. The directions of linear polarization and of the axes of circular polarization are parallel to the magnetic field.

Let us consider the case of a linearly-polarized component. Let the incident wave be plane and linearly polarized in such a way that the angle between the electric intensity of the incident wave and the applied magnetic field is θ . Experiments on the inverse Zeeman effect (and the classical theory of the Zeeman effect) indicate that the probability of absorbing a quantum from the wave is proportional to $\cos^2 \theta$.

In the case of circularly-polarized components conditions are very similar to those of linear polarization, the only difference being that the "radiation" emitted is circularly polarized. According to the Principle of Correspondence, the probability of the absorption of a linearly-polarized wave by a circularly-polarized component must be related to the probability of the absorption of a circularly-polarized wave by the same component in a manner similar to that in which the component would absorb on the classical theory. For equal energies, therefore, a wave linearly polarized with the electric vector perpendicular to the magnetic field gives a

* Wood, 'Researches in Physical Optics,' pt. ii. p. 174 (Columbia University Press, 1919).

probability of absorption of a quantum which is only one-half of what it would be if the wave were circularly polarized. More generally if the wave normal P and the electric vector E be chosen as a system of polar coordinates θ, ϕ (θ = complement of latitude measured from E ; ϕ = longitude measured from P in a plane perpendicular to E) to which we refer the magnetic field H , then the circular vibration "corresponding" to the circularly-polarized Zeeman component may be broken up into two equally intense linear components at right angles to each other and 90° out of phase. For the directions of resolution we choose $\left(\frac{\pi}{2} + \theta, \phi\right)$ and $\left(\frac{\pi}{2}, \phi + \frac{\pi}{2}\right)$. The second of these is not affected by E , being at right angles to it. The first, when resolved along E , becomes multiplied by $\sin \theta$. Since its intensity is one-half of the intensity of the circular vibration, the probability of absorption is $\frac{1}{2} \sin^2 \theta$ on the same scale as that in which the probability of absorption of a quantum from a linearly-polarized wave is $\cos^2 \theta$ if θ is the angle between the directions of polarization of the wave and of the linear Zeeman component (H). Before passing on to the numerical calculations involving (I), we must consider the meaning of (I) in more detail.

The numbers a, b, c, \dots refer to intensities observed in a direction perpendicular to the applied magnetic field. The components c, β, d, γ are linear and the remaining ones are circular. It is clear that the total energy sent out in the form of the circular components is underestimated by a factor of 2 on account of the inefficient angle at which these components are observed in comparison with the linear components. The probabilities of transitions are therefore proportional to

$$2a, 2b, c, 2a, \beta \dots \dots \dots (I')$$

for equal times of remaining in the excited levels.

If the atom has been excited to the level x (fig. 1), the probability of returning to the lower energy state is 1 during any appreciable time. Thus the probability of the emission of the component (b) is simply proportional to the probability of the excitation of x . This level is excited by absorbing b when the atom is in the lower of the two equally probable ($1s$) levels. Letting θ be (as before) the angle between the electric intensity of the incident wave and the applied magnetic intensity, the probability of the absorption of b is $2b \frac{\sin^2 \theta}{2} = b \sin^2 \theta$, and this, therefore, is also the probability

of its re-emission. On the light-quantum theory the lateral emission of b has then a probability equal to that of the re-emission of b .

If the atom has been excited to the level (y), it may return to ($1s$) along a or d . The probabilities of these two returns are to each other as $2a$ is to c (since d, c are symmetrical), and since the total probability of a return is certainty, these two probabilities are $\frac{2a}{2a+c}$ and $\frac{c}{2a+c}$. Just as in the case of b , the probability of absorbing a is $a \sin^2 \theta$ and that of absorbing c is $c \cos^2 \theta$, the total probability of reaching y being therefore $a \sin^2 \theta + c \cos^2 \theta$, and the probabilities of radiating a and c are

$$\frac{2a}{2a+c} (a \sin^2 \theta + c \cos^2 \theta)$$

and

$$\frac{c}{2a+c} (a \sin^2 \theta + c \cos^2 \theta).$$

Similarly for α and β these quantities are $\alpha \sin^2 \theta$, $\beta \cos^2 \theta$,

$$\frac{2\alpha}{2\alpha+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta),$$

$$\frac{\beta}{2\alpha+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta).$$

Fig. 3.



Let the line of sight be perpendicular to the plane of the paper in fig. 3, H remaining in the direction θ, ϕ . We shall need in what follows the relative proportions of light polarized along E and along P . The linear components contribute:

$$\cos^2 \theta \text{ along } E$$

and

$$\sin^2 \theta \cos^2 \phi \text{ along } P.$$

The circular Zeeman components may be first broken up into two equal parts along $\left(\frac{\pi}{2} + \theta, \phi\right)$ and $\left(\frac{\pi}{2}, \phi + \frac{\pi}{2}\right)$, the

intensity of each being $\frac{1}{2}$ of the intensity of the whole. The first of these gives $\frac{1}{2} \sin^2 \theta$ along E and $\frac{1}{2} \cos^2 \theta \cos^2 \phi$ along P. The second gives 0 along E and $\frac{1}{2} \sin^2 \phi$ along P, giving for both (since their phase-difference is $\frac{\pi}{2}$) $\frac{1}{2} \sin^2 \theta$ along E and $\frac{1}{2} (\sin^2 \phi + \cos^2 \theta \cos^2 \phi)$ along P. The two amounts are therefore :

$$\begin{aligned}
 E &= \left[\frac{2a}{2a+c} (a \sin^2 \theta + c \cos^2 \theta) + \frac{2a}{2a+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta) \right. \\
 &\quad \left. + b \sin^2 \theta \right] \frac{\sin^2 \theta}{2} + \left[\frac{c}{2a+c} (a \sin^2 \theta + c \cos^2 \theta) \right. \\
 &\quad \left. + \frac{\beta}{2a+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta) \right] \cos^2 \theta, \\
 P &= \left[\frac{2a}{2a+c} (a \sin^2 \theta + c \cos^2 \theta) + \frac{2a}{2a+\beta} (\alpha \sin^2 \theta + \beta \cos^2 \theta) \right. \\
 &\quad \left. + b \sin^2 \theta \right] \cdot \frac{1}{2} (\sin^2 \phi + \cos^2 \theta \cos^2 \phi) \\
 &\quad + \left[\frac{c}{2a+c} (a \sin^2 \theta + c \cos^2 \theta) + \frac{\beta}{2a+\beta} (\alpha \sin^2 \theta \right. \\
 &\quad \left. + \beta \cos^2 \theta) \right] \sin^2 \theta \cos^2 \phi.
 \end{aligned}$$

Case I. Let E, P, H be as in fig. 3, the line of sight being perpendicular to the plane of the figure. We want to know the state of polarization. We have $\theta = \frac{\pi}{2}$, $\phi = 0$. From the expressions for E and P it follows that

$$\frac{E-P}{E+P} = \frac{\frac{b}{2} - \frac{a(c-a)}{2a+c} - \frac{\alpha(\beta-\alpha)}{2a+\beta}}{\frac{b}{2} + \frac{a(c+a)}{2a+c} + \frac{\alpha(\beta+\alpha)}{2a+\beta}} = 0.30.$$

Wood and Ellett record 30 per cent. polarization.

Case II. Let E, P be as in Case I., but let H be parallel to E in fig. 3. Using the values of E and P and letting $\theta = 0$, we have

$$\frac{E-P}{E+P} = \frac{\frac{c(c-a)}{2a+c} + \frac{\beta(\beta-\alpha)}{2a+\beta}}{\frac{c(c+a)}{2a+c} + \frac{\beta(\beta+\alpha)}{2a+\beta}} = 0.14.$$

It appears from the article of Wood and Ellett that the

polarization in this case was not much weaker than in Case I. It thus appears that the theory of light quanta gives a too small value for the polarization. However, no definite statement as to the amount of polarization is made by Wood and Ellett.

Case III. Wood and Ellett observed that if H is in the plane of E and P, and if $\theta = 45^\circ$, the polarization disappears. There is no polarization if the intensities of the circular components are equal to the intensities of linear components. This means :

$$\tan^2 \theta = \frac{\frac{c(c-a)}{2a+c} + \frac{\beta(\beta-\alpha)}{2\alpha+\beta}}{\frac{b}{2} - \frac{a(c-a)}{2a+c} - \frac{\alpha(\beta-\alpha)}{2\alpha+\beta}}, \quad \theta = 31^\circ.$$

This differs from 45° by an amount greater than can be accounted for by experimental error. The discrepancy indicates perhaps the presence of influences enhancing C, B at the expense of other components. The handing-on of radiation may be suspected as such an influence.

Case IV. Let E be perpendicular to the plane of the paper in fig. 3, and H have the direction shown in the figure. The vapour is sensitive to the circular components only, and thus the case is not different from I.

Case V. Let E be as in IV., and H parallel to the position of E in fig. 3. Again only the circular excitation takes place. Hence the same result as in I.

Case VI. Positions of H intermediate between IV. and V. give the same result; the direction of polarization simply rotates with the field.

The behaviour deduced in IV., V., VI. is the observed behaviour. The observations on mercury in a field of reasonable strength appear to fit into the same scheme. Of course, all disturbing influences (collisions, secondary resonance radiation, light scattered by the walls of the bulb) will cause depolarization.

2. Polarization in Sodium in a Weak Field or in the absence of an External Field.

Let the magnetic field have no definite orientation, and let all directions of the field be equally probable. Suppose also that the variations in the field are slow in comparison with the time of excitation. Then the resultant polarization can be obtained by averaging the expressions for E and P.

We obtain

$$\frac{E-P}{E+P} = \frac{\frac{2(\alpha-c)^2}{2\alpha+c} + \frac{2(\alpha-\beta)^2}{2\alpha+\beta} + b}{7(\alpha+\alpha+b) + 3(c+\beta) + \frac{c(c-\alpha)}{2\alpha+c} + \frac{\beta(\beta-\alpha)}{2\alpha+\beta}} = 0.055.$$

Wood and Ellett (*l. c.*) observed 5 per cent. polarization in the absence of a magnetic field for sodium.

We have supposed in the above calculation that the magnetic field does not change its direction during a time long enough to allow the atom to absorb the incident radiation and then to re-emit it again. This supposition is, of course, itself questionable, and its validity depends upon experimental conditions. It is difficult to suppose that the magnetic field is of an intermolecular nature because the time during which two atoms are likely to be sufficiently close to each other to act with a field of 100 gauss is likely to be only 10^{-11} sec., whereas the time of excitation is of the order of 10^{-8} sec.

On the other hand, if the magnetic field during emission should have a random distribution of directions with respect to the field during absorption, and if the atom should be affected by both fields in its quantization, then the radiation must be entirely unpolarized.

3. Polarization of Mercury Vapour in the absence of a Magnetic Field.

If considerations similar to those applied to sodium should be carried through for mercury, similar results would be obtained, whereas Wood and Ellett find 90 per cent. polarization in the absence of a magnetic field. This result is very puzzling inasmuch as it seems to imply that the incident wave has orienting influence on the "corresponding" radiating mechanism. If this "corresponding" mechanism is linear, the axis of vibration is to be thought of as directed along the electric vector of the incident wave. If the mechanism is circular, the plane of vibration is to be thought of as perpendicular to the wave normal. A differentiation between the two mechanisms could be obtained by examining the radiation in directions oblique to the incident beam. Such observations, however, are not available.

The possibility of simultaneous actions by two atoms in this case cannot be postulated unless it is also supposed to be fundamental when the magnetic field is present, for otherwise the intensities observed with and without the field would be different.

It must be remarked, however, that the application of the Principle of Correspondence in the above discussion is only tentative. Thus one cannot deny the possibility of a correspondence between the whole phenomenon of resonance radiation: (a) on the classical theory, (b) on the theory of quantized levels. If, then, the Hg atom should correspond to a classical linear resonator performing a forced oscillation, complete polarization would result.

We see from the amounts of polarization recorded by Wood and Ellet that the quantization of Hg in a magnetic field does not appear to hold when H is less than 2 gauss. (In sodium a field of the order of 100 gauss was required.) Without attempting to see what happens for these small fields, one can suppose that their magnitude is such that the Larmor precession* has a period which is too long in comparison with the average time τ during which the mercury atom remains in the excited state. In a field of two gauss the Larmor precession has a period of roughly 3×10^{-7} sec.; the assumption is that the quantization is diffuse if the atom returns to the normal state in a time comparable with the period of this precession—that is, the quantum conditions cannot be applied to a coordinate unless that coordinate *actually passes* through changes of a periodic character.

The experiments of Franck and Cario† and of Cario‡ support the view that, if all the collisions are effective in removing energy from excited Hg atoms, the time τ is of the order 10^{-8} sec. Wood§, however, gives $\frac{1}{15600}$ sec. as the time required for the appearance of the green fluorescent radiation when mercury vapour is illuminated at a pressure of 2.5 mm. This is the time between two collisions bringing about fluorescence. Taking the mean free path at 760 mm. pressure as 1.6×10^{-5} cm. and the mean velocity as 1.7×10^4 cm./sec., the interval between collisions at 2.5 mm. is roughly 3×10^{-7} sec., while Wood obtains 6×10^{-5} sec. One might suppose, therefore, that collisions bringing about fluorescence are 100 times more rare than ordinary collisions. If this result may be extended to the case of Hg resonance radiation, and if the pressure-effects discussed by Cario and by Cario and Franck are to be left unchanged, their time τ must be multiplied by about 100; the resulting value is of the order of magnitude of the Larmor precession for two

* See *Atombau*, 3rd ed., p. 364.

† *Zs. f. Phys.* xi. p. 161 (1922).

‡ *Zs. f. Phys.* x. p. 185 (1922).

§ *Proc. Roy. Soc. A*, xcix. p. 362 (1921).

gauss. Wood* has described experiments in which secondary resonance radiation in Hg was photographed with a quartz plate inserted at the edge of the primary beam. Under these conditions no excited molecules from the primary beam can travel into the region of the secondary radiation, and the entire secondary effect is due to radiation which has passed through the quartz plate. On comparing the photograph with one taken in the absence of the quartz plate, it was found that the decrease in intensity of the secondary radiation was about 25 per cent., while loss by reflexion at the plate is about 10 per cent. Thus it is probable that a portion of the secondary radiation is due to atoms which travel out of the path of the primary beam, and by measuring the width of the secondary strip an estimate of the time τ can be obtained. Wood's value is about 10^{-5} sec. This result has been questioned by Stern† on the basis that the reflexion power of the quartz may have been underestimated. So far as we know, the question is still unsettled, but the probability is that the time τ is actually considerably larger than 10^{-8} sec.

For Na, the classical estimate of $\tau = 10^{-8}$ sec. is in agreement with the order of magnitude of the period of the Larmor precession for 100 gauss, which is the field used by Wood and Ellett‡. This suggests that the difference in τ of Hg and Na is due to the fact that $\lambda 2536$ of Hg is a combination line and that classical estimates are not applied to it as readily as to ordinary lines. The behaviour of Hg in a magnetic field observed by Franck and Grotrian§ shows that something not considered in the above discussion is brought about by the magnetic field; of course, the experiment of Franck and Grotrian had reference to the fluorescent molecular radiation.

* *Phys. Zeit.* xiv. p. 177 (1913). The author's attention has been called to these experiments and their criticism by Stern, by Mr. A. E. Ruark.

† *Phys. Zeit.* xx. p. 183 (1919).

‡ It must be pointed out that the behaviour of D_1 and D_2 for separate excitation observed by Wood and Mohler (*Phys. Rev.*, n.s., xi. p. 70, 1918) points toward a larger value for τ , say 5×10^{-6} sec. For the small energy transfer between D_1 and D_2 it may be that the atoms are to be considered as colliding even when at a considerable distance apart. A factor of ten in the radius causes a factor of 100 in the mean free path and in the collision interval. Stern (*l. c.*) has pointed out that excited atoms have larger diameters than normal ones, and that this must be taken into account in estimates of collision intervals. Cario has utilized this fact in his estimates of τ (*l. c.*).

§ *Zs. f. Phys.* vi. p. 35 (1921).

Summary.

A quantitative elaboration of the consequences of the Zeeman effect in resonance radiation gives polarizations in fair agreement with observed values of Wood and Ellett, for sodium in a strong magnetic field and in the absence of a field.

The value of H which suffices to establish the space quantizing appropriate to a magnetic field is tentatively brought into connexion with the period of the Larmor precession as compared with the time constant τ of the atom. Numerical agreement is attained in the case of mercury if $\tau \cong 10^{-6}$ sec. rather than 10^{-8} sec. Evidence in favour of $\tau \cong 10^{-6}$ sec. is adduced; it is suggested that not all collisions are effective in causing fluorescent emission, since this also explains the measurements of Wood on the time lag of fluorescence in mercury vapour. The case of sodium is treated on the assumption that $\tau \cong 10^{-8}$ sec.

Mr. A. E. Ruark, of the Johns Hopkins University and of the National Bureau of Standards, is responsible for the thought that the Zeeman effect may account for the polarization of resonance radiation. He has also contributed most generously to the improvement of every part of this paper, having checked through the calculations and gone over the experimental evidence. The writer's sincerest thanks are due to him for this assistance.

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LXXXI. *The Charging Effect produced by the Rotation of a Prolate Iron Spheroid in a Uniform Magnetic Field.* By ERNEST LAWRENCE, M.A.*

Introduction.

PROFESSOR W. F. G. SWANN† has discussed the interpretation of the "Moving-Line Theory" of electromagnetic induction which is consistent with Maxwellian theory for the case of a symmetrically magnetized system rotating about the axis of symmetry. At a subsequent time he carried out an experiment confirming these conclusions

* Communicated by Prof. W. F. G. Swann.

† Swann, Phys. Rev. (2) xv. pp. 365-398 (1920); Phys. Rev. (2) xix. p. 381 (1922).

for the case of a rotating magnetized sphere. For reasons which will appear later it was deemed worth while to repeat the experiment for a prolate spheroid rotating and magnetized symmetrically about its major axis. The theoretical formulæ for an ellipsoid were worked out by Dr. Rognley*, of this department, and the present experiment forms a verification of his results.

Theoretical Considerations.

The theory immediately involved in the experiment may be briefly summarized as follows :—

The force acting on an electron is

$$\text{where} \quad \mathbf{F} = \mathbf{E} + \frac{[\mathbf{V}\mathbf{H}]}{C}$$

$$\mathbf{E} = -1/C \frac{\partial \bar{U}}{\partial t} - \text{Grad } \phi,$$

\mathbf{U} and ϕ being the usual vector and scalar potentials, respectively, while \mathbf{E} and \mathbf{H} are the electric and magnetic

vectors. For the case of a rotating spheroid $\frac{\partial \mathbf{U}}{\partial t}$ is zero by

symmetry so that \mathbf{E} is derivable from a potential. It is found that the scalar potential ϕ is of the type resulting from an electrostatic polarization giving rise to a fictitious volume and surface distribution of electricity. It follows,

neglecting the so-called "Motional Intensity" $\frac{[\mathbf{V}\mathbf{H}]}{C}$, that

the electrons in the magnet will redistribute themselves so that the electric field at all points will be zero. The "Motional Intensity" will cause a further rearrangement of the electrons which will in general alter the potential of internal and external points. In this manner the potential of the axis of the spheroid is altered by rotation, so that when the axis is earthed a charge comes to the ellipsoid. The potential of a metal shell surrounding the rotating system would be altered as a result of the appearance of such a charge, resulting in the movement of the spot of an attached electrometer system. Dr. Rognley showed this alteration of potential to be :

$$\Delta V = - \frac{4\pi n B b^2}{3C} q_{12}/q_{22}, \quad . \quad . \quad . \quad (1)$$

where B is the total magnetic induction in the spheroid, b the minor axis, and the q 's are the usual coefficients of

* Rognley, Phys. Rev. (2) xix. p. 609 (1922).

capacity and induction, the subscripts 1 and 2 referring to the spheroid and shell (with attached electrometer system), respectively. n is the number of revolutions per second and C is the velocity of light.

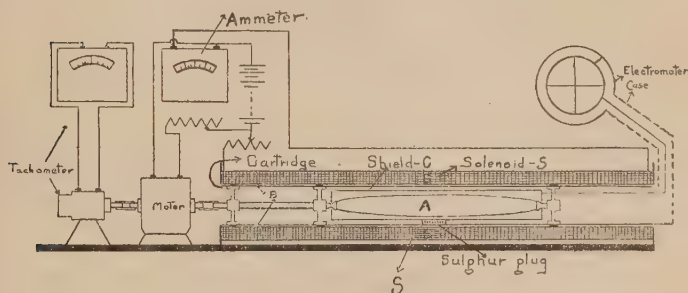
It is of interest to here note that B is the total magnetic induction in the iron. Dividing the induction into two parts, one associated with the magnetization of the spheroid and the other with the external field, a plausible but erroneous view would be one in which the lines of the former field rotated with the spheroid and produced no electrical effects, while the lines of the latter field produced the full effect calculated from (1)—with B replaced by the external field. For the ellipsoid used, such a view leads to a value for ΔV of the order of magnitude of three per cent. of the value given by the correct theory referred to above. The experiment on the rotation of a sphere provided a conclusive test of the theory, but there the difference between the conclusions of the correct and the erroneous theory amounted to a factor of only three while in the case of the rotation of a prolate spheroid the difference amounts to a factor of thirty. The experiment has a further interest in that it is a representative of a class of experiments which have been performed before but in which such effects as might have been obtained were screened off on account of the particular arrangement of apparatus used.

Experimental Procedure.

Fig. 1 indicates the details of the apparatus. An ellipsoid A of mild steel having minor axis two centimetres and major axis twenty centimetres was mounted on brass shafting, the shafting being soldered to the extremities of the ellipsoid. Bearings for the shafting were mounted in a brass tube B having a removable cover; and ellipsoid and shaft were mounted therein, in such a manner as to be readily accessible through the cover. A shell C , cylindrical in shape, was mounted on sulphur, so as to surround the ellipsoid in the tube. It was so designed as to be readily opened for access to the ellipsoid. The tube assembly thus described will henceforth be referred to as the "cartridge." A solenoid S , of such dimensions as to produce a uniform saturation magnetomotive force over the ellipsoid, when the cartridge was inserted therein, was made by winding number 10 copper wire on a brass tube slightly larger than the cartridge tube. The cartridge was inserted in the solenoid and the shaft connected to a high-speed motor which also was connected to a Hopkins Electric Tachometer. The quadrant of a

Dolezalek electrometer was connected directly to the shell in the cartridge, the cartridge tube, bearings, etc., being connected to the case of the electrometer system. Suitable rheostats provided means of regulating the speed of the motor and the current flow in the solenoid. A ballistic galvanometer calibrated by a Hibbert Standard was used in the determination of fluxes in the ellipsoid.

Fig. 1.



The ellipsoid was set in rotation, and the speed adjusted by a rheostat to the value desired. At the same time the current in the solenoid was adjusted to a definite value and the motion of the electrometer spot was watched. The tachometer dial and ammeter were so placed as to enable the experimenter to keep close check on all three readings simultaneously. The current and speed were adjusted continually and the moment it was evident that the electrometer spot was steady and the current and speed had the desired values, the position of the spot was noted. Then, immediately, the current in the solenoid was reversed by the throw of a commutator switch, and again the operation of adjusting current, speed, etc., was carried out and the reading of the deflected spot was taken. A second reversal of current with a like process of observation brought the spot back to approximately the first reading. This set of operations was repeated three to five times, according as the readings were deemed reliable. Next the current was changed to another value and the above procedure repeated. Measurements were made in this manner for four different currents, and with four different speeds of rotation for each value of the current.

It was found that there existed at intervals a drift of the electrometer needle which was attributed to thermocouple effects in the solenoid interior, as it was noted that the rate

of drift increased with the temperature of the solenoid interior. This fact, incidentally, made it necessary to take the cartridge out after each run of observations and cool it in order that the drift should be kept at a minimum.

The ratio q_{12}/q_{22} was determined as follows: The ellipsoid was insulated in its bearings by paper. The shell-electrometer system was insulated with the ellipsoid earthed, and the latter was then raised to a potential V_1 . The shell rose in consequence to a potential V_2 which, since the shell and electrometer were both insulated, is related to V_1 by

$$q_{12}V_1 + q_{22}V_2 = 0.$$

Thus, it is only necessary to know V_1 and V_2 in order that the q ratio be known. If θ_1 is the electrometer deflexion corresponding to the potential V_1 and θ_2 the deflexion which results from applying a potential V_2 to the quadrant, it follows that

$$\frac{\theta_1}{\theta_2} = \frac{V_1}{V_2} = -q_{22}/q_{12},$$

which serves to determine q_{12}/q_{22} .

The mean of four determinations gave $q_{12}/q_{22} = -0.235$.

The electrometer sensitivity was determined in the usual manner, namely, by applying a known potential and noting the deflexion resulting therefrom. Determinations of the sensitivity taken throughout the range of the scale involved in the experiment showed that variation from proportionality of potential and deflexion was negligible.

The determination of the fluxes through the ellipsoid corresponding to the various currents in the solenoid presented difficulties requiring close attention. The ballistic galvanometer was mounted at a sufficient distance from the solenoid to ensure that stray fluxes produced errors of less than one per cent. Since the magnetic induction B is determined by dividing the total number of maxwells cut by the total area of the turns of wire wound on the ellipsoid enclosing the flux, it was necessary to ascertain the cross-sectional area of the ellipsoid at the point with considerable care, as an error of 0.5 millimetre in the measurement of the radius of the circular cross-section of the ellipsoid enclosed by the wire corresponded to an error of 5 per cent. in the final result. The galvanometer was calibrated from the throws of a Hibbert Standard Coil, which had itself been previously calibrated to within a tenth of one per cent.

Results.

A complete tabulation of data and results obtained is of little importance and too lengthy to print, and it will suffice to give a resumé of the final results embodied in the following table.

No. of Observations.	Speed R.P.M.	B E.M.U.	Volts ($\times 10^{-2}$) Observed.	Volts ($\times 10^{-2}$) Calculated.	Difference per cent.
4	2400	14,900	2.37	2.37	0.0
4		16,500	2.69	2.64	+1.9
4		19,100	3.09	3.04	+1.6
3	3200	14,900	3.19	3.18	+0.3
4		16,550	3.54	3.52	+0.5
4		17,950	3.78	3.82	-1.0
3		19,100	4.03	4.06	-0.7
4	4000	16,550	4.55	4.40	+3.4
5		17,950	4.87	4.77	+2.0
5	4800	17,950	5.74	5.72	+0.4
3		19,100	6.04	6.10	-1.0

The first column numbers indicate the number of observations for the particular set of conditions of speed and magnetic induction indicated in the second and third columns for which the change in potential of the fourth column represents the mean. The fifth column gives the theoretical value for the change in potential which is the object of verification.

The average discrepancy between the calculated and observed values estimated regardless of sign is 1.2 per cent. while the greatest deviation is 3.4 per cent. In view of the smallness of the quantities measured and the exceptional conditions attendant with high rotational velocities and large magnetic fluxes, the results as set forth may be considered a satisfactory experimental confirmation of the theoretical formula.

The writer wishes to take this opportunity to express his sincere thanks to Prof. W. F. G. Swann, who assigned the problem, for his continued interest and advice. He wishes also to express appreciation of the services of Mr. C. Dane, the laboratory mechanic, and Mr. W. B. Haliday, who aided in setting up the apparatus.

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Sept. 29, 1923.

LXXXII. *The Anhysteretic Qualities of Iron and Nickel and the Energy Change at the Critical Temperature.* By J. R. ASHWORTH, D.Sc.*

INDEX TO PARAGRAPHS.

1. Development of an equation to anhysteretic curves of $I=\phi(H)$.
 2. Experiments to trace anhysteretic isothermals.
 3. Results obtained with iron and the determination of R_1 and its relation to R' .
 4. Determination of the ferromagnetic field Constant a_1 ; Relation of R' , a' and R_1 , a_1 .
 5. Results obtained with nickel and the values of R_1 and a_1 .
 6. Corresponding states for $I=\phi(H)$.
 7. Relation of R_1 to I_0 .
 8. Energy change in passing from ferromagnetism to paramagnetism
 9. Table of constants and equations.
1. **A** FERROMAGNETIC substance above its critical temperature behaves as a paramagnetic body and obeys the simple law expressed by the equation

$$\frac{H}{I} = R' T, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where H is the applied magnetic field, I the intensity of magnetization, treated as magnetic moment per unit volume, T the absolute temperature, and R' a constant which is the reciprocal of Curie's constant (the product of the magnetic susceptibility and the absolute temperature). This equation as written above implies that the intensity of magnetization may increase indefinitely with the magnetizing field, which conflicts with the fact that the intensity has a limit. The equation must therefore be extended to include this fact and we write it as follows:—

$$H \left(1 - \frac{1}{I_0} \right) = R' T, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where I_0 is the limiting or maximum intensity of magnetization.

In order to pass from paramagnetism to ferromagnetism two other facts must be recognized: first, that the intensity of magnetization becomes 10^6 to 10^7 times larger than in the paramagnetic state and secondly, that hysteresis is in general in evidence. Both these facts may be incorporated

* Communicated by the Author.

in the equation if a term $a'I^2$ be added to H , which is equivalent to the addition of an intrinsic field, and we write,

$$(H + a'I^2) \left(\frac{1}{I} - \frac{1}{I_0} \right) = R'T, \quad . \quad . \quad . \quad (3)$$

which is an equation applying to ferromagnetic susceptibility. By multiplying all through by I_0^2 and writing R for $R'I_0^2$ *, we obtain the energy equation to ferromagnetism, which may conveniently be put,

$$(HI_0 + a'I_0I^2) \left(\frac{I_0}{I} - 1 \right) = RT. \quad . \quad . \quad . \quad (4)$$

The first bracket represents energy in terms of magnetic quantities, the second bracket represents the fractional part of that energy, and the quantity RT has the same significance as in the gas equation and expresses thermal energy.

Reverting to equation (3), it has been shown† that it is only an extremely small part of the intrinsic field which is a genuine magnetic field, and that the larger part, which is indeed approximately the whole, is of another kind and makes its appearance in virtue of energy considerations. The intrinsic field is therefore of a dual nature and a' , the constant of this field, must be separated into two parts, a_1 for the magnetic part and c for the other part, so that $a' = a_1 + c$; but inasmuch as a_1 is negligible compared with c we shall not make an appreciable error in putting a' for c .

We now write equation (3) in two parts as follows:—

$$(H + a_1I^2) \left(\frac{1}{I} - \frac{1}{I_0} \right) = R_1T \quad . \quad . \quad . \quad (5)$$

$$\text{and} \quad a'I^2 \left(\frac{1}{I} - \frac{1}{I_0} \right) = R'T. \quad . \quad . \quad . \quad (6)$$

Here in equation (5) we have replaced R' in equation (3) by R_1 in order to give suitable values when the non-magnetic field is omitted, and the equation then involves only magnetic quantities and is applicable to ferromagnetism when H and I are the variables. In equation (6) we have written a' for c and have omitted H , which is in general negligible compared with $a'I^2$ (except at temperatures above the critical temperature when I becomes very small), and the equation then applies to $I=f(T)$.

* For nickel $R/2$ must be written for R —see *Phil. Mag.* vol. xxxvi. p. 351.

† *Phil. Mag.* vol. xliii. p. 401.

If, in equation (5), we suppress magnetic hysteresis in any of the recognized ways, then the term $a_1 I^2$ disappears, and the equation for anhysteretic isothermals is

$$H\left(\frac{1}{I} - \frac{1}{I_0}\right) = R_1 T. \quad \dots \quad (7)$$

It is analogous to the complete equation to paramagnetism (equation (2)) and only differs from it in that R_1 replaces R' .

It becomes a matter of theoretical interest to find values for the coefficients a_1 and R_1 in the ferromagnetic equation (5) and to compare them with a' and R' .

2. We have seen that the suppression of hysteresis eliminates the unknown quantity a_1 and equation (7), which then results, involves only the unknown quantity R_1 . We begin, therefore, by tracing anhysteretic curves at constant temperatures for the determination of R_1 .

In a former investigation* such curves were traced for iron and nickel at different temperatures and the suppression of hysteresis was effected by running an alternating current through the magnetic material all the time it was under examination; this method was suitable for bringing out certain general features which were then being investigated, but it yields values for the intensity of magnetization which are lower than the truth and the results so obtained cannot be used here.

An easy and effective method of suppressing hysteresis is to heat the ferromagnetic material, at any given field strength, above its critical temperature and allow it to cool to the required temperature. This procedure was now adopted with this modification: instead of heating and cooling at each step of the magnetizing process, a set of curves at a number of different field strengths was plotted as the specimen cooled after being raised above its critical temperature, and from these curves another set was constructed, each curve giving the anhysteretic values of I for different field strengths at some one temperature.

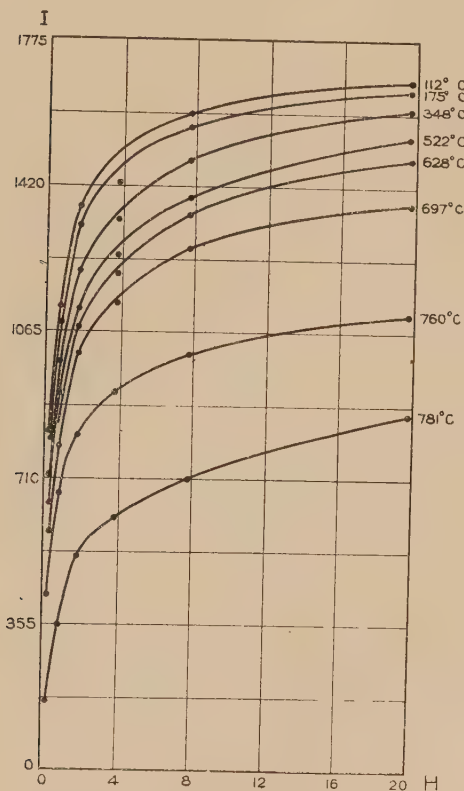
The experiments were made on well annealed wires of iron and nickel, the iron wire being 18.9 cm. in length and 0.056 cm. in diameter, and the nickel wire 19.0 cm. in length and 0.088 cm. in diameter; they were inserted singly in a long solenoid and the intensity of magnetization was determined by a sensitive astatic mirror magnetometer. In

* Ashworth, *Phil. Mag.* xxvii. p. 357 (Feb. 1914).

general the arrangements for heating and the other details of the experiment were the same as those described in the paper on the "Anhyseretic properties of Iron and Nickel," to which reference has been made*.

3. Diagram I. exhibits anhyseretic curves of iron

Diagram I.—Anhyseretic isothermals of Iron.



determined in this way from cooling curves. Applying the equation

$$H \left(\frac{1}{I} - \frac{1}{I_0} \right) = R_1 T$$

to these anhyseretic curves we find for the most probable

* Phil. Mag. xxvii. p. 357 (Feb. 1914).

values of R_1 , at the temperatures given below, the following numbers :—

C°.	A°.	$R_1 \times 10^6$.
112	385	0.67
175	448	0.64
348	621	0.57
370	643	0.57
522	795	0.54
628	901	0.53
760	1033	0.62

$$\text{Mean} = 0.59 \times 10^{-6}$$

Each of the values of R_1 has been arrived at by selecting five or six points on the curve and treating the equations formed from them by the method of least squares. Corrections for self-demagnetization have been made. The mean value 0.6×10^{-6} for R_1 receives confirmation from an experiment by Ewing* on the magnetization of very soft annealed iron wire under vibration by tapping. He remarks that under these circumstances an initial permeability of about 80,000 is found and, treating the air temperature at which the experiment was made as 15° C., this gives a value for R_1 of 0.55×10^{-6} .

The paramagnetic constant R' , which is the reciprocal of Curie's constant, is 3.56 when the intensity of magnetization is treated as magnetic moment per unit volume, and we have therefore for the ratio of R' to R_1 ,

$$\frac{R'}{R_1} = \frac{3.56}{0.6} \times 10^6 = 5.9 \times 10^6.$$

The kinetic energy of two degrees of freedom per unit of temperature per cubic centimetre of iron is

$$R = \frac{83.2 \times 10^6}{55.85} \times 7.86 = 11.7 \times 10^6,$$

the atomic weight of iron being 55.85 and the density 7.86, and the number just found for the ratio of R' to R_1 is almost exactly the half of this, so that numerically we have

$$\frac{R'}{R_1} = \frac{R}{2} \dots \dots \dots (8)$$

* Ewing, 'Magnetic Induction in Iron and other Metals,' p. 115, 1894.

4. Having obtained a value for R_1 , we can now make a determination of a_1 . If in the ferromagnetic hysteresis equation

$$(H + a_1 I^2) \left(\frac{1}{I} - \frac{1}{I_0} \right) = R_1 T,$$

we put H equal to zero, then I is the residual intensity of magnetization (I_r) and we get

$$a_1 I_r^2 \left(\frac{1}{I_r} - \frac{1}{I_0} \right) = R_1 T. \quad . \quad . \quad . \quad . \quad (9)$$

But we may also write, when the residual magnetism is regarded as a function of the temperature,

$$a' I_r^2 \left(\frac{1}{I_r} - \frac{1}{I_0} \right) = R' T;$$

and it follows that

$$\frac{a'}{a_1} = \frac{R'}{R_1}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and therefore

$$a_1 = a' \frac{R_1}{R'}.$$

The values on the right-hand side of this equation are :

$$a' = 7.00, \quad R' = 3.56, \quad R_1 = 0.6 \times 10^{-6},$$

and consequently

$$a_1 = 1.2 \times 10^{-6}.$$

It follows from equation (10) that

$$\frac{a'}{a_1} = \frac{R}{2},$$

since

$$\frac{R'}{R_1} = \frac{R}{2}.$$

There is another method which allows a_1 to be estimated, and may be used to corroborate the result just obtained. The anhyseretic equation, when the intensity of magnetization has the residual value I_r , is

$$H \left(\frac{1}{I_r} - \frac{1}{I_0} \right) = R_1 T,$$

and the hysteretic equation is

$$a_1 I_r^2 \left(\frac{1}{I_r} - \frac{1}{I_0} \right) = R_1 T$$

when H is zero. By division we get

$$H = a_1 I_r^2,$$

and therefore

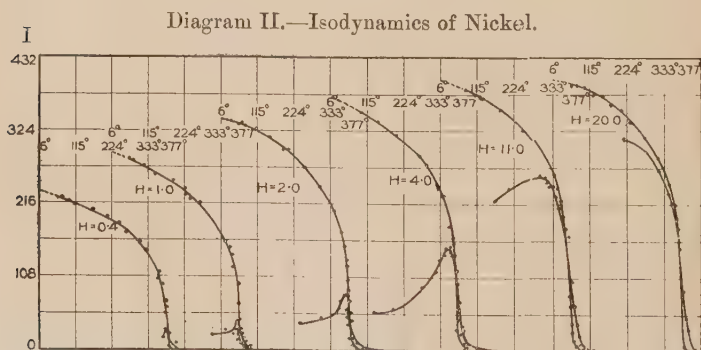
$$a_1 = \frac{H}{I_r^2}.$$

Observations give $H = 2.0$ on the anhysteretic curve when $I_r = 1350$. Hence

$$a_1 = \frac{2.0}{1350^2} = 1.1 \times 10^{-6}.$$

This method of determining a_1 involves the square of the residual intensity, and the probable error in the evaluation of a_1 is larger than in the first method. The former result, 1.2×10^{-6} , is for this reason to be preferred.

5. Experiments made on nickel in the same way as on iron yield results of a like kind. Anhysteretic curves of



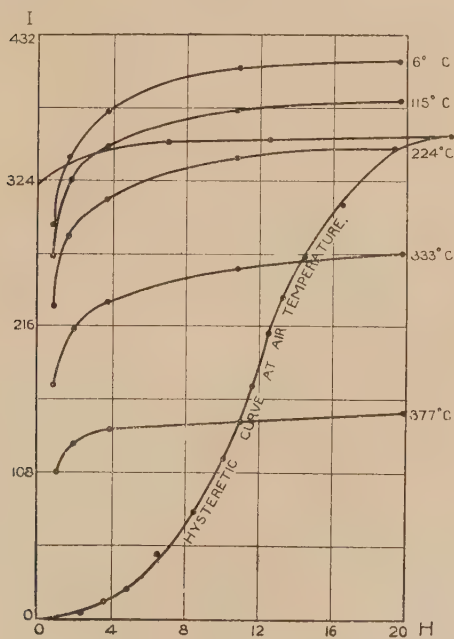
nickel, derived from the isodynamic curves of Diagram II., corrected for self-demagnetization, are shown in Diagram III., and from these and others, not shown in the diagram, the

following values of R_1 at the subjoined temperatures are derived :—

C°.	A°.	$R_1 \times 10^6$.
6	279	3.11
107	380	3.09
115	388	2.69
200	473	2.35
224	497	2.35
292	565	3.78
333	606	3.61
377	650	4.23

Mean 3.15×10^{-6}

Diagram III.—Anhyseretic isothermals of Nickel.



R' for nickel, calculated from Curie's constant, is 20.8 and the ratio of R' to R_1 is

$$\frac{R'}{R_1} = \frac{20.8}{3.2} \times 10^6 = 6.5 \times 10^6.$$

The constant R for nickel, obtained in the same way as for iron, is 12.6×10^6 , and the half of this, namely 6.3×10^6 , is nearly the ratio of $\frac{R'}{R_1}$, and so again we have

$$\frac{R'}{R_1} = \frac{R}{2} \dots \dots \dots (11)$$

6. The determination of a_1 may be made from the equation

$$\frac{a'}{a_1} = \frac{R'}{R_1}.$$

Putting $R_1 = 3.2 \times 10^{-6}$ as above, $a' = 83.7$ and $R' = 20.8$, we get

$$a_1 = 13.3 \times 10^{-6}.$$

For the corroboration of this value, we may use the alternative method which was employed in this connexion with iron. We then have

$$a_1 = \frac{H}{I_r^2},$$

where H is the anhysteretic value of the field for intensity equal to I_r .

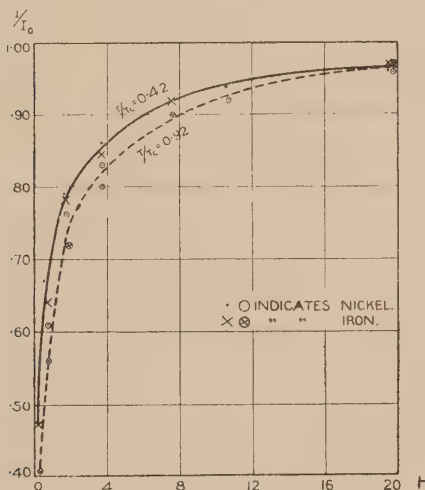
In Diagram III. a hysteretic curve has been traced in addition to the anhysteretic curves, and from this I_r is found to be 320 and the corresponding anhysteretic field is 1.3 units. Hence

$$a_1 = 12.7 \times 10^{-6}.$$

6. The equations of both iron and nickel have the same general form and they differ only in having different constants. By constructing a reduced equation for each of these metals the theory of corresponding states should then apply. In Diagram IV. anhysteretic reduced values of the intensity of magnetization, calculated as a fraction of the value at absolute zero and at a field-strength of 20 units, have been marked on the vertical axis, and *observed* field-strengths on the horizontal axis. It is sufficient to mark observed field strengths because calculation shows that the critical field is the same in magnitude for iron and nickel and their reduced field strengths must therefore be the same for any observed field strength. It is, however, necessary to use reduced temperatures as the critical temperatures of iron and nickel are not the same, and this has been done.

Points from an anhyseretic curve of iron at 175° C. have been plotted along with points from an anhyseretic curve of nickel at 6° C., these temperatures being corresponding temperatures and having a reduced value of 0.42; and it will be seen that a single curve runs evenly through all of them. Similarly another single curve at the reduced temperature of 0.92, which corresponds to 697° C. for iron and 333° C. for nickel, runs evenly through reduced anhyseretic values of intensity of magnetization. Thus the principle of corresponding states applies to anhyseretic curves of $I=\phi(H)$ for iron and nickel.

Diagram IV.—Curves $I/I_0=\phi(H)$ at reduced temperatures for Iron and Nickel.



7. It has been shown in a former paper* that the maximum intensity of magnetization (I_0) can be successfully calculated from the equation

$$R = R' I_0^2 \quad \dots \dots \dots (12)$$

when iron is the ferromagnetic material. Also, we have found above by equation (8) that

$$R = 2 \frac{R'}{R_1},$$

* "On the Calculation of Magnetic and Electric Saturation Values," Phil. Mag. xxxvi. p. 351 (October 1918).

and it at once follows that

$$\frac{2}{R_1} = I_0^2.$$

Numerically, we have

$$\frac{2}{R_1} = \frac{2}{0.6} \times 10^6 = 3.3 \times 10^6,$$

$$I_0^2 = 1817^2 = 3.3 \times 10^6.$$

Thus with iron,

$$R_1 I_0^2 = 2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

When nickel is the ferromagnetic material equation (12) must be written

$$\frac{R}{2} = R' I_0^2,$$

and this combined with (11) leads to

$$\frac{1}{R_1} = I_0^2.$$

The numerical verification is

$$\frac{1}{R_1} = \frac{1}{3.2} \times 10^6 = 0.31 \times 10^6,$$

$$I_0^2 = 552^2 = 0.305 \times 10^6.$$

Thus with nickel,

$$R_1 I_0^2 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

8. The expression $R_1 I_0^2$ relates to the energy per unit of temperature in the ferromagnetic state below the critical temperature, while $R' I_0^2$ is the energy per unit of temperature above the critical temperature. Now R_1 is negligible compared with R' and therefore it follows that the change of energy per unit of temperature on passing through the critical temperature is $R' I_0^2$. This is equal to R for iron and $R/2$ for nickel and hence we may say:—

When iron or nickel passes through the critical temperature there is a change of kinetic energy per unit of temperature equivalent to that of *two degrees of freedom*, the molecular weight of iron being 55.85 and that of nickel 2×58.68 above the critical temperature.

This change of energy is found to be simply and intimately connected with the discontinuity of the true specific heat at the critical temperature.

9. A table of the symbols used in this paper and their numerical values together with some of the more important relations subsisting between them is subjoined.

		IRON.	NICKEL.
Critical Temperature	T_c	1058° A	661° A
Maximum Intensity of Magnetization ...	I_0	1817	552
Paramagnetic Constant	R'	3.56	20.8
Intrinsic Field Constant	α'	7.0	83.7
Ferromagnetic Constant	R_1	0.6×10^{-6}	3.2×10^{-6}
Ferromagnetic Field Constant	a_1	1.2×10^{-6}	13.3×10^{-6}
Gas Constant.....	R	11.7×10^6	12.6×10^6
True Specific Heat at the Critical Temperature	c_θ	0.309	0.154

EQUATIONS :—

	IRON.	NICKEL.
$T_c = \frac{8}{27} \frac{\alpha' I_0}{R'}$	$R' I_0^2 = R.$	$R' I_0^2 = \frac{R}{2}.$
$R_1 = \frac{R'}{R/2}.$	$R_1 I_0^2 = 2.$	$R_1 I_0^2 = 1.$
$a_1 = \alpha' \frac{R_1}{R'} = \frac{\alpha'}{R/2}.$		

LXXXIII. *An Automatic Feeder for Coloured Flames.* By J. J. MANLEY, M.A., Research Fellow, Magdalen College, Oxford*.

IN a former paper † a simple device was described for maintaining the coloured flames required for polarimetric and spectroscopic work. Recent experiments with replicas of the original apparatus have shown that in general it is difficult to establish the conditions required for a slow and uniform flow of salt solution through the platinum wire wick. When the flow is not suitably restricted, considerable spurting occurs: this is not only highly inconvenient, but also harmful to adjacent instruments. These defects are

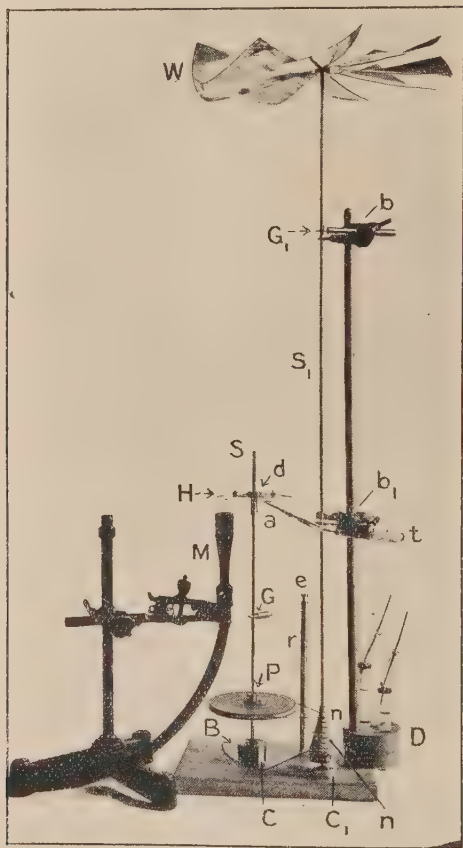
* Communicated by the Author.

† Phil. Mag. xlv. p. 336 (Feb. 1923).

not experienced with the new and more elaborate automatic feeder illustrated in fig. 1.

The base of the feeder is an ordinary iron retort-stand having a rectangular foot 20 cm. long and 13 cm. wide and a rod 60 cm. high. Two bosses, b , b_1 , are clamped to

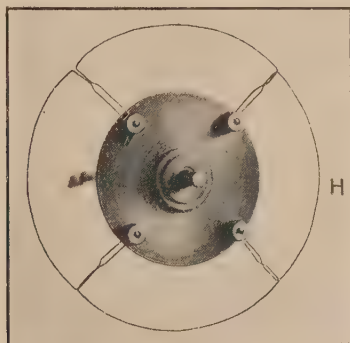
Fig. 1.



the rod; the one, b , carries a brass guide G_1 for the steel rod S_1 , and the other, b_1 , a tubular holder for the glass reservoir t , containing the salt solution for colouring the flame. The upper end of S_1 is fitted with eight inclined and curved sectors of aluminium: the lower end is glass-hard and sharply pointed, and it rests within a conical oil-charged hole in a brass block C_1 screwed to the base. This part of the apparatus is therefore very similar to that used for

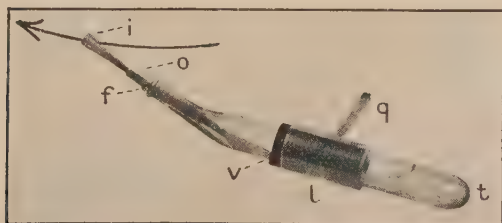
actuating the stirrer in an Ostwald thermostat. S is another steel rod similar to but shorter than S_1 : its hardened point also rests within a brass oil-containing cup C soldered to the plate B . The rod is supported by the guide G , which, after adjustment, is fastened by the screw e . Attached to S

Fig. 2.



are (1) a light pulley P_1 , cord driven by any one of the several pulleys formed upon the boxwood cone n , and (2) a brass disk d fitted with screw bolts and nuts; these hold the ends of the four radiating arms of a platinum wire ring H (fig. 2). The supporting rod r passes first through the brass plate B to which it is soldered, and then through the hole in the iron base: in this position it is stiffly held by a washer and nut. Thus the plate B , with r as a pivot, can be turned to the right or left, and the tension of the driving-cord thereby diminished or increased. A large burner of

Fig. 3.



the Meker or Fisher type is placed with its top 1 or 2 cm. below the platinum-wire ring. The glass reservoir t and its holder l are, for the sake of clearness, shown detached in fig. 3. The neck of the reservoir contains a loosely-fitting glass wick holder o having a small bulb f resting within

the lipped opening. The wick *i* is of silky and compact asbestos fibre, rendered pliable by drawing it between the thumb and fore finger; it is broadened out at *i* to ensure continuous contact with the platinum-wire ring. The rubber band *v* prevents the reservoir from slipping in its holder; the arm *q* is held by the boss *b* (fig. 1). The feeder is adjusted and brought into use in the following way:—

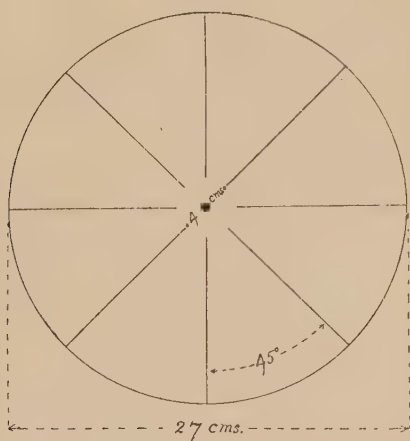
First, the apparatus is placed at a suitable distance from the spectroscope or polarimeter and the height of the platinum-wire ring adjusted; the ring is then secured to *S* by a screw beneath the disk. Next, the reservoir *t* is inclined until the wick becomes effective; it is then raised or lowered, and slued round until the flat portion of the wick bears tangentially and lightly upon the outside of the platinum ring and with its top pointing in the direction of the receding wire, as shown by the arrowed line in fig. 3. Finally, the Bunsen burner is placed as already described, and at a distance of 4 cm. from the wick. On kindling the gas, the hot air ascending from the flame actuates the vane system above, with the result that the platinum ring is continuously rubbed by the salt-charged wick and passed through the flame, thus producing a non-intermittent and intense coloration. As the successive portions of the ring are still hot when they again reach the wick, a more or less dry residue is carried into the flame: in this way any spurring is altogether negligible. When not in use, the reservoir is placed in an upright position by suitably rotating the arm *q* (fig. 3). The wire ring is cleaned by continuing the application of the flame after the removal of the wick. For convenience, several reservoirs each containing a different salt solution may be prepared. Idle reservoirs are placed in the circular apertures of the block *D* (fig. 1), through which the iron rod of the stand passes and to which it affords support.

For those desiring to construct automatic feeders for their own use, the following additional details may be helpful. And here we remark that the best results are obtained only when the several moving parts of the apparatus are given certain relative dimensions. If, for example, the vane system *W* is too small, the speed is excessive; also the driving-power is insufficient to overcome the friction between the wire and the wick. The dimensions named below have proved entirely satisfactory.

1. *The Vanes*.—The driving system is made from an aluminium disk 27 cm. in diameter and 0.5 mm. thick.

The disk is cut into eight equal sectors, as shown in fig. 4; the cuts terminate at points 2 cm. from the centre. The sectors are turned so as to form an angle of about 45° with the original plane surface and then gently curved, as seen in fig. 1. Made thus, the system possesses considerable strength, and is not readily distorted or damaged. In these

Fig. 4.



respects it is superior to the usual Ostwald pattern, which is built up from individual sections of much thinner sheet; moreover, rivetting is entirely avoided.

2. *The Rods S, S₁.*—These are of tool steel 4 mm. in diameter. Suitable lengths are 35 cm. for S and 75 for S₁: the former enables one to adjust the height of the platinum ring for almost any spectroscope or polarimeter without the aid of blocks. The length of S₁ places the vanes well above, and out of the way of other apparatus.

3. *The Disk d.*—This is 46 mm. in diameter and 1 mm. thick. It is drilled at four equidistant points near the edge for the reception of small screw bolts and nuts, as shown in fig 2. (No. 8 B.A. bolts are convenient.)

4. *The Platinum-wire Ring.*—The ring is formed from one

Fig. 5.



piece of wire 40 cm. long and 0.5 mm. in diameter. First, the wire is bent as indicated in fig. 5, and then made

approximately circular, with the four twinned arms directed towards the centre. Next, the inner extremities of the arms are secured by their respective nuts, and the wire ring is made truly circular. Prepared thus, the ring has a diameter of about 8 cm. Additional rigidity is imparted by bending and crossing the twinned arms, as seen in fig. 2. If the arms are bent gently downwards they are not traversed by the solution from the wick.

5. *The Pulleys*.—The pulley P is 9 cm. in diameter and 7 mm. or less thick; it is of mahogany and well covered with shellac varnish. The boxwood cone *n* tapers from a diameter of 26 mm. to one of 8 mm. Eight grooves are cut in it, and these range in diameter from 22 to 5 mm. The groove 8 mm. in diameter gives excellent results; with it the wire makes three revolutions per minute: its velocity is therefore 12 mm. per second.

6. *The Driving-cord*.—The driving-cord should be chosen with care. After trying various cords, a single thread of Manilla hemp composed of some four to six fibres was found superior to all others. The thread is glossy and tough and not easily frayed; and as its diameter is about 0.3 mm. only, the knot formed by tying the ends is too small to disturb the smooth running of the apparatus.

6. *The Reservoirs*.—These are conveniently made from glass tubing 12 mm. in diameter. The body may be 8 cm. and the neck 3 cm. long.

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LXXXIV. *On Mr. T. Smith's Formulæ for Oblique Focal Distance in Terms of Magnification.* By ALICE EVERETT, M.A. (*From the National Physical Laboratory.*)*

NEAR the end of a paper on Ray Tracing (Proc. Phys. Soc. vol. xxx. p. 232, 1918) Mr. T. Smith gives, merely incidentally and without proof, new formulæ for finding the position of either member of a pair of conjugate primary foci in terms of the magnification, on a ray traced through a coaxial lens system. The present writer has had occasion to employ these formulæ, and, since results based on statements of which no proof has been published may be regarded as incomplete, ventures here to offer a proof of her

* Communicated by the Author.

own, together with some remarks on the corresponding formulæ for secondary foci by the same author (*Ibid.* vol. xxvii. p. 508, 1915).

Preliminary Note on some Properties of certain Sequence Formulæ employed in the Proof.

Suppose p'_λ , q'_λ and p''_λ , q''_λ to be representative terms of two different series of quantities both satisfying the following relations

$$p_\lambda = a_\lambda p_{\lambda-1} - b_{\lambda-1} q_{\lambda-1}, \quad q_\lambda = c_\lambda q_{\lambda-1} + d_\lambda p_\lambda \quad . \quad . \quad (1)$$

then it is known that

$$\frac{p'_\lambda q''_\lambda - p''_\lambda q'_\lambda}{p'_{\lambda-1} q''_{\lambda-1} - p''_{\lambda-1} q'_{\lambda-1}} = a_\lambda c_\lambda, \quad . \quad . \quad (2)$$

regardless of the values of the b 's and d 's. This can easily be proved by actual substitution.

Hence

$$\frac{(p'q'' - p''q')_\lambda}{(p'q'' - p''q')_1} = \prod_{\lambda=2}^{\lambda=n} a_\lambda c_\lambda, \quad . \quad . \quad (3)$$

Π signifying continued product.

Corollary.—If $a_\lambda = c_\lambda = 1$ for all values of λ , then

$$(p'q'' - p''q')_\lambda = \text{constant} = p'_1 q''_1 - p''_1 q'_1. \quad . \quad (3A)$$

It is evident that p_λ , q_λ can be written in the forms

$$p_\lambda = a_\lambda p_0 + \beta_\lambda q_0, \quad q_\lambda = \gamma_\lambda p_0 + \delta_\lambda q_0.$$

Hence, when $q_0 = 0$, we have $p_\lambda = p_0 a_\lambda$, $q_\lambda = p_0 \gamma_\lambda$;

and when $p_0 = 0$, we have $p_\lambda = q_0 \beta_\lambda$, $q_\lambda = q_0 \delta_\lambda$.

Clearly a_λ and γ_λ are the values of p_λ and q_λ when $p_0 = 1$ and $q_0 = 0$; and β_λ , δ_λ are the values of p_λ , q_λ when $p_0 = 0$, $q_0 = 1$.

Hence, when $q_0 = 0$,

$$\left. \begin{aligned} p_\lambda &= p_0 (\text{value of } p_\lambda \text{ for } p_0 = 1), \\ q_\lambda &= p_0 (\quad , \quad , q_\lambda \quad , \quad , \quad); \\ \text{and when } p_0 &= 0, \\ p_\lambda &= q_0 (\text{value of } p_\lambda \text{ for } q_0 = 1), \\ q_\lambda &= q_0 (\quad , \quad , q_\lambda \quad , \quad , \quad). \end{aligned} \right\} . \quad . \quad . \quad (4)$$

Nomenclature.

The quasi-differential notation of the original has been renounced for reasons of economy, and some other slight alterations of nomenclature have been found expedient.

The letters employed have the following significations:—

$\phi_\lambda, \phi'_\lambda$ are the angles of incidence and refraction at the λ th surface.

ψ_λ is the inclination of the ray to the optic axis after λ refractions.

μ_λ is the refractive index of the λ th medium.

t_λ is the length of path in the λ th medium.

$k_\lambda = k'_\lambda \cos \phi_\lambda \cos \phi'_\lambda = (\mu_\lambda \cos \phi'_\lambda - \mu_{\lambda-1} \cos \phi_\lambda) / r_\lambda$.

p_λ, q_λ for the axial section are the distances of object and image points from the λ th surface, measured along the ray in the direction light travels. (The object point here is the image formed by the previous $\lambda - 1$ surfaces. p and q here have nothing to do with the p and q in the preliminary note, and will not be used in a way likely to cause confusion.)

P is the value of p_1 for $q_n = \infty$.

Q is the value of q_n for $p_1 = -\infty$.

$\eta_\lambda, \eta'_\lambda$ are the perpendiculars from the λ th point of incidence upon the consecutive ray in the axial section before and after incidence.

m is the magnification perpendicular to the ray of a linear element in the axial section.

P and Q may be otherwise defined as the distances of the principal oblique foci along the ray from the first and last surfaces of the lens.

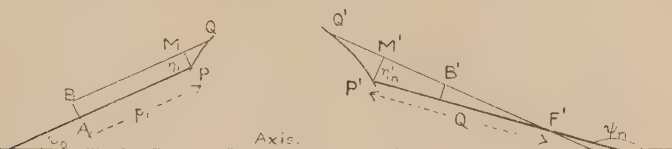
In discussing the sagittal section, and secondary foci, p, q, P, Q are replaced by u, v, U, W , and m by ν .

I. Formulee for the Primary Focal Distances.

The discussion of the primary foci is confined to rays in an axial plane.

In the figure, $AP \dots P'A'F'$ is the chief ray, F' the second principal oblique focus. BMQ is a very near ray parallel to AP ; therefore its path $Q'B'$ after refraction passes through F' . P, Q are the points of incidence of the two rays, and P', Q' their points of emergence. $PM = \eta_1$ and $P'M' = \eta'_n$ are drawn perpendicular from P, P' to the near ray. $AB = \eta_1$ is a line

element perpendicular to the incident ray; $A'B'$ is drawn from A' , the image of A , perpendicular to the refracted chief ray.



Then m , the magnification in the axial plane, is defined as the ratio of $A'B'$ to AB .

Let $P'F' = Q$, $AP = p_1$, $P'A' = q_n$.
Then

$$AB = PM = \eta_1, \quad A'B' = P'M' \frac{A'F'}{P'F'} = \eta'_n \frac{(Q - q_n)}{Q};$$

$$\therefore m = \frac{A'B'}{AB} = \frac{\eta'_n (Q - q_n)}{\eta_1 Q}. \quad \text{Also } Q d\psi_n = -\eta'_n;$$

$$\therefore q_n = Q - m \frac{Q\eta_1}{\eta'_n} = \frac{-\eta'_n}{d\psi_n} + m \frac{\eta_1}{d\psi_n}.$$

If $\eta_\lambda, \eta'_\lambda$ be the perpendiculars from the point of intersection of the chief ray with the λ th surface upon the consecutive ray before and after incidence, and ds the element of arc PQ , then $\eta'/\cos \phi' = \eta/\cos \phi = ds$ for any value of λ .

Hence, substituting for η'_n , we have

$$\frac{q_n}{\mu_n} = - \left(\frac{\eta}{\mu_n d\psi} \cdot \frac{\cos \phi'}{\cos \phi} \right)_n + \frac{m\eta_1}{\mu_n \cdot d\psi_n} \dots \dots (5)$$

Similarly, if instead of taking $d\psi = 0$ (*i. e.* the incident rays parallel), we take $d\psi_n = 0$ (*i. e.* the emergent rays parallel), we obtain

$$\frac{p_1}{\mu_0} = - \left(\frac{\eta'_1}{\mu_0 d\psi_0} \cdot \frac{\cos \phi_1}{\cos \phi'_1} \right) + \frac{\eta'_n}{m\mu_0 d\psi_0} \dots \dots (6)$$

Now $\eta_\lambda - \eta'_{\lambda-1} = t_{\lambda-1} \cdot d\psi_{\lambda-1};$

$$\therefore \eta_\lambda - \eta_{\lambda-1} \frac{\cos \phi'_{\lambda-1}}{\cos \phi_{\lambda-1}} = t_{\lambda-1} d\psi_{\lambda-1} \dots \dots (7)$$

and

$$\eta'_{\lambda-1} - \eta'_\lambda \frac{\cos \phi_\lambda}{\cos \phi'_\lambda} = -t_{\lambda-1} d\psi_{\lambda-1} \dots \dots (8)$$

Also
$$k_\lambda \cdot ds_\lambda = k'_\lambda \eta_\lambda \cos \phi'_\lambda = k'_\lambda \eta'_\lambda \cos \phi_\lambda$$

$$= (\mu_\lambda \cos \phi'_\lambda - \mu_{\lambda-1} \cos \phi_\lambda) d(\phi' - \psi)_\lambda$$

$$= \mu_\lambda \cos \phi'_\lambda (d\phi'_\lambda - d\psi_\lambda) - \mu_{\lambda-1} \cos \phi_\lambda (d\phi_\lambda - d\psi_{\lambda-1}),$$

since
$$\phi'_\lambda - \phi_\lambda = \psi_\lambda - \psi_{\lambda-1},$$

$$= -\mu_\lambda \cos \phi'_\lambda d\psi_\lambda + \mu_{\lambda-1} \cos \phi_\lambda d\psi_{\lambda-1},$$

because

$$\mu_\lambda \cos \phi'_\lambda d\phi'_\lambda - \mu_{\lambda-1} \cos \phi_\lambda d\phi_\lambda$$

$$= d(\mu_\lambda \sin \phi'_\lambda - \mu_{\lambda-1} \sin \phi_\lambda) = 0;$$

i. e.,
$$\mu_\lambda d\psi_\lambda - \mu_{\lambda-1} d\psi_{\lambda-1} - \frac{\cos \phi_\lambda}{\cos \phi'_\lambda} = -k'_\lambda \eta_\lambda, \quad . \quad . \quad . \quad (9)$$

$$\mu_{\lambda-1} d\psi_{\lambda-1} - \mu_\lambda d\psi_\lambda \frac{\cos \phi'_\lambda}{\cos \phi_\lambda} = k'_\lambda \eta'_\lambda. \quad . \quad . \quad . \quad (10)$$

(7) and (9) may be used to find η_n and $\mu_n d\psi_n$ in (5); and (8) and (10) to find η'_1 and $\mu_0 d\psi_0$ in (6), calculating in the reverse direction.

Either pair of equations (7, 9) or (8, 10) is of the type (1) mentioned in the preliminary note, $-\eta$ corresponding to p , and $\mu d\psi$ to q . Hence by (4), if $d\psi_0 = 0$, and G_λ, H_λ denote the special values of $-\eta_\lambda, \mu_\lambda d\psi_\lambda$ given by (7) and (9) for the initial value $-\eta_0 = 1$, then the values of $-\eta_\lambda, \mu_\lambda d\psi_\lambda$ for any initial value of η are

$$-\eta_\lambda = -\eta_0 G_\lambda \quad \text{and} \quad \mu_\lambda d\psi_\lambda = -\eta_0 H_\lambda.$$

We assume $\eta_1 = \eta_0$, since the initial rays are parallel, and any imaginary surface crossed by the ray before it reaches the first surface would cause no refraction. Thus

$$-\eta_\lambda = -\eta_1 G_\lambda \quad \text{and} \quad \mu_\lambda d\psi_\lambda = -\eta_1 H_\lambda.$$

Incidentally it may be mentioned that, corresponding to the values $-\eta_0 = 1, \mu_0 d\psi_0 = 0$, equations (7) and (9) give $-\eta_1 = 1, \mu_1 d\psi_1 = k'_1$.

From the values just found for $-\eta_\lambda, \mu_\lambda d\psi_\lambda$, it follows that

$$\frac{-\eta_n}{\mu_n d\psi_n} = \frac{G_n}{H_n}, \quad \frac{-\eta_1}{\mu_1 d\psi_1} = \frac{1}{H_n}.$$

Inserting these values in (5), it becomes

$$\frac{q_n}{\mu_n} = \frac{G_n \cos \phi'_n}{H_n \cos \phi_n} - \frac{m}{H_n}. \quad . \quad . \quad . \quad (11)$$

Treating (6) on similar lines, but reckoning backwards and starting with $-\eta'_n, \mu_n d\psi_n = 0$ as initial quantities, it becomes

$$\frac{p_1}{\mu_0} = -\frac{G_1' \cos \phi_1}{H_n \cos \phi_1'} + \frac{1}{m H_n}, \quad (12)$$

where G_1', H_n are the values of $-\eta_1', \mu_0 d\psi_0$ that would be obtained if $-\eta'_n = 1, \mu_n d\psi_n = 0$. G_n, G_1', H_n are ray constants. (11) and (12) are Mr. T. Smith's formulæ.

It may perhaps be instructive to compare the foregoing with the following analysis.

From the well-known formula for refraction at a single (the λ th) surface,

$$\frac{\mu_\lambda \cos^2 \phi'_\lambda}{q_\lambda} - \frac{\mu_{\lambda-1} \cos^2 \phi_\lambda}{p_\lambda} = k_\lambda,$$

where $p_\lambda = q_{\lambda-1} - t_{\lambda-1}$, it is evident (and may be proved by induction) that q_λ is of the form

$$\frac{A_\lambda + C_\lambda p_1}{B_\lambda + D_\lambda p_1}.$$

This expression, however, does not give neat results, and we therefore take new variables:

$$p'_\lambda = \frac{1}{\mu_{\lambda-1}} \left(\frac{p}{\epsilon \cos^2 \phi} \right)_\lambda, \quad q'_\lambda = \left(\frac{q}{\mu \epsilon \cos^2 \phi'} \right)_\lambda,$$

leaving the significance of the constant ϵ for future consideration, and write

$$q'_\lambda = \frac{E_\lambda + G_\lambda p'_1}{F_\lambda + H_\lambda p'_1} \dots \dots \dots (13)$$

Substituting the corresponding expression for $q'_{\lambda-1}$ in the equation of refraction, and comparing coefficients in the two expressions for q'_λ , we find the following relations between the G 's and H 's,

$$\left. \begin{aligned} f'_\lambda G_\lambda &= G_{\lambda-1} \epsilon_{\lambda-1} \cos^2 \phi'_{\lambda-1} - \left(H \frac{t}{\mu} \right)_{\lambda-1}, \\ f'_\lambda H_\lambda &= H_{\lambda-1} \epsilon_\lambda \cos^2 \phi_\lambda + (k \epsilon G)_\lambda, \end{aligned} \right\} \dots \dots (14)$$

where f'_λ is another undetermined constant. Similar relations connect the E 's and F 's.

(13) is equivalent to

$$\left(q'_\lambda - \frac{G_\lambda}{H_\lambda}\right)\left(p'_1 + \frac{F_\lambda}{H_\lambda}\right) = \left(\frac{EH - FG}{H^2}\right)_\lambda. \quad (15)$$

It is desirable to select the constants ϵ and f so as to give a convenient expression for $EH - FG$ in (15), besides rendering the equations (14) as simple as possible.

By (3)

$$\frac{(EH - FG)_\lambda}{(EH - FG)_1} = \frac{\left(\prod_{\lambda=1}^{Lt=n} \frac{\epsilon_\lambda}{f_\lambda} \cos \phi_\lambda \cos \phi'_\lambda\right)^2}{\epsilon_1 \epsilon_\lambda \cos^2 \phi_1 \cos^2 \phi'_\lambda}.$$

A glance shows that matters will be simplified by putting

$$f_\lambda = 1, \quad \frac{1}{\epsilon_\lambda} = \cos \phi_\lambda \cos \phi'_\lambda.$$

Equations (14) then become

$$\left. \begin{aligned} G_\lambda &= G_{\lambda-1} \frac{\cos \phi'_{\lambda-1}}{\cos \phi_{\lambda-1}} - \left(H \frac{t}{\mu}\right)_{\lambda-1}, \\ H_\lambda &= H_{\lambda-1} \frac{\cos \phi_\lambda}{\cos \phi'_\lambda} + k'_\lambda G_\lambda, \end{aligned} \right\} \quad \dots \quad (16)$$

where $k' = k\epsilon$, and are the same as (7) and (9) above with G written for $-\eta$ and H for $\mu d\psi$.

Also

$$\frac{(EH - FG)_\lambda}{(EH - FG)_1} = \frac{\cos \phi'_1 \cdot \cos \phi_\lambda}{\cos \phi_1 \cdot \cos \phi'_\lambda},$$

or

$$(EH - FG)_\lambda \frac{\cos \phi'_\lambda}{\cos \phi_\lambda} = \text{constant for all values of } \lambda.$$

As regards initial values, the equation of refraction gives

$$q'_1 = \frac{p'_1}{1 + k'_1 p'_1},$$

and hence

$$E_1 = 0, \quad F_1 = 1, \quad G_1 = 1, \quad H_1 = k'_1.$$

Hence replacing q' , p' by their values in terms of the original q , p , (15) yields

$$\left(q_n - \frac{G_n}{H_n} \cdot \frac{\cos \phi'_n}{\cos \phi_n}\right)\left(p_1 + \frac{F_n}{H_n} \cdot \frac{\cos \phi_1}{\cos \phi'_1}\right) = -\frac{1}{H_n^2} \dots \quad (17)$$

If we reverse the order, and, instead of expressing q'_λ in terms of p'_λ as in (13), express p'_λ in terms of q_n , putting

$$p'_\lambda = \frac{E'_\lambda + G'_\lambda q'_n}{F'_\lambda - H'_\lambda q'_n},$$

we obtain in a similar manner relations between the G' 's and H' 's like (8) and (10). $H'_1 = H_n$, and we get the following equation instead of (17):

$$\left(\frac{q_n}{\mu_n} - \frac{F'_1}{H_n} \frac{\cos \phi'_n}{\cos \phi_n} \right) \left(\frac{p_1}{\mu_0} + \frac{G'_1}{H_n} \frac{\cos \phi_1}{\cos \phi'_1} \right) = - \frac{1}{H_n^2}. \quad (18)$$

II. Formule for the Secondary Focal Distances.

The following is an alternative discussion of the case of the sagittal section:—

Taking the optic axis as axis of x ,

let y_0, z_0 be coordinates of the object point P,

y_n, z_n „ „ „ „ secondary focus Q,

Y_1, Z_1 „ „ „ „ point of incidence,

Y_n, Z_n „ „ „ „ „ „ emergence,

M_0, N_0 „ „ „ „ „ „ direction cosines of the incident ray,

M_n, N_n „ „ „ „ „ „ emergent ray,

u „ „ the distance of the object point from the lens
along the ray,

v „ „ the distance of the secondary focus from the lens
along the ray,

ν „ „ the magnification.

When the ray is in an axial plane, conjugate line elements perpendicular to the ray in the sagittal section are proportional to their distances from the optic axis. For a ray

not in an axial plane, we define ν by $\nu = \sqrt{\frac{y_n^2 + z_n^2}{y_0^2 + z_0^2}}$.

The salient characteristic of a pair of secondary foci for a single surface is that the line joining them passes through the centre. Hence in a coaxial system all successive secondary foci lie in the axial plane through the object point. The equation of an axial plane through P is $yz_0 = zy_0$. Expressing the fact that Q lies on this plane, we have

$$\frac{y_n}{y_0} = \frac{z_n}{z_0} = \sqrt{\frac{y_n^2 + z_n^2}{y_0^2 + z_0^2}} = \nu.$$

Also

$$\begin{aligned} y_1 - Y_1 &= M_0 u, & y_n - Y_n &= M_n v, \\ z_1 - Z_1 &= N_0 u, & z_n - Z_n &= N_n v. \end{aligned}$$

Thus, if ν is given, we have six equations connecting the six quantities y_0, z_0, y_n, z_n, u, v . By straightforward elimination we can get rid of y_0, z_0, y_n, z_n , and obtain two equations in u and v , whence

$$u(M_0N_n - N_0M_n) = -(Y_1N_n - Z_1M_n) + \frac{1}{\nu}(Y_nN_n - Z_nM_n), \quad (19)$$

$$v(M_0N_n - N_0M_n) = (Y_nN_0 - Z_nM_0) - \nu(Y_1N_0 - Z_1M_0). \quad (20)$$

In this form the rays are not applicable to rays in the plane $z=0$. The ratios of the coefficients must be reduced to a form which does not become indeterminate in that case.

Now, by the well-known law of refraction, we have

$$\mu_\lambda M_\lambda - \mu_{\lambda-1} M_{\lambda-1} = -k_\lambda Y_\lambda$$

and evidently

$$Y_\lambda - Y_{\lambda-1} = \frac{t_{\lambda-1}}{\mu_{\lambda-1}} (\mu M)_{\lambda-1}.$$

Two similar relations connect Z and N .

Suppose C_n, K_n to be final values given by the sequence equations

$$K_\lambda - K_{\lambda-1} = k_\lambda C_\lambda$$

$$C_\lambda - C_{\lambda-1} = -\left(\frac{t}{\mu} K\right)_{\lambda-1},$$

for initial values $C_0=1, K_0=0$.

Then by (4)

$$\mu_n M_n = -Y_1 K_n; \quad Y_n = Y_1 C_n; \quad \mu_n N_n = -Z_1 K_n, \quad Z_n = Z_1 C_n;$$

$$\therefore \mu_n (M_0 N_n - N_0 M_n) = K_n (Y_1 N_0 - M_0 Z_1),$$

$$Y_n N_0 - Z_n M_0 = C_n (Y_1 N_0 - M_0 Z_1).$$

Hence, cutting out the factor $Y_1 N_0 - Z_1 M_0$ in each term, (20) becomes

$$\frac{\nu}{\mu_n} = \frac{C_n - \nu}{K_n}.$$

Similarly, supposing C'_1 and $K'_1 = K_n$ to be values given by

$$C'_{\lambda-1} - C'_\lambda = \left(\frac{t}{\mu} K'\right)_{\lambda-1},$$

$$K'_{\lambda-1} - K'_\lambda = -k_\lambda C'_\lambda,$$

starting with $C'_n=1, K'_n=0$, and working backwards, then we find values for the first two coefficients of (19) containing $Y_n N_n - Z_n M_n$ as a factor; and on cutting out this factor the

equation reduces to

$$\frac{u_1}{\mu_0} = -\frac{C'_1}{K_n} + \frac{1}{\nu K_n}.$$

The second method adopted above becomes much simpler in the case of the secondary foci. The equation of refraction is

$$\frac{\mu_\lambda}{v_\lambda} - \frac{\mu_{\lambda-1}}{u_\lambda} = k_\lambda.$$

By putting in turn

$$v_\lambda = \frac{A_\lambda + C_\lambda u_1}{B_\lambda + K_\lambda u_1} \quad \text{and} \quad u_\lambda = \frac{A'_\lambda + C'_\lambda v_n}{B'_\lambda - K'_\lambda v_n},$$

and equating coefficients in two expressions as before in the case of the primary foci, we arrive at relations between the coefficients C, K and C', K' of exactly the same form as in the paraxial case, the only difference being that the paraxial t and k are replaced by those defined above under "*Nomenclature*."

LXXXV. *A Consequence of the Theory of M. Louis de Broglie.*
(Phil. Mag., February 1924, p. 446.)

M. DE BROGLIE'S formula :

$$h\nu = \frac{m_0 c^2}{\sqrt{1-\beta^2}}$$

gives

$$\beta = \sqrt{1 - \frac{m_0^2 c^4}{h^2 \nu^2}},$$

or

$$v = c \sqrt{1 - \frac{m_0^2 c^4}{h^2 \nu^2}}.$$

M. de Broglie estimates m_0 as being of the order of 10^{-50} gr. Let us take a vibrator with a period of $T = 726\frac{2}{3}$ sec. If we put in de Broglie's formula $m_0 = 10^{-50}$, $c = 3 \cdot 10^{10}$, $h = 6 \cdot 54 \cdot 10^{-27}$, and $\nu = \frac{1}{T} = \frac{1}{726\frac{2}{3}} = \frac{3}{2180}$, the result will be

$$v = 0.$$

The velocity of the waves is zero! Our vibrator cannot emit electromagnetic waves! Likewise the inductive effect in a transformer of an alternating current with a period of $T = 726\frac{2}{3}$ sec. must be equal to zero. It would be interesting to examine the question experimentally.

Dorpat,
27th February, 1924.

WILHELM ANDERSON.

LXXXVI. *The Arc Spectrum of Phosphorus.*By M. O. SALTMARSH, B.A., *F.Inst.P.***Introduction.*

THE wave-lengths of a large number of lines in the spectrum of phosphorus, produced under a variety of conditions, have been measured by Geuter † over the range λ 5728– λ 2390 A.U. The only lines which occurred in the spectrum of a carbon arc to which a compound of phosphorus had been added were two pairs in the ultra-violet between λ 2555 and λ 2534. These were also produced in a discharge through phosphorus vapour in a vacuum tube. They are recorded by De Gramont ‡ as being the persistent rays of phosphorus. Three triplets and several pairs of constant frequency difference have been noted by Paulson § in the spectrum of phosphorus in the region from λ 5500 to λ 3348. The radiation and ionization potentials of phosphorus have been measured by Foote and Mohler ||.

Phosphorus is an element of group V of the periodic table, and no series relationships have yet been worked out for any of these elements. Multiplets have recently been found in the spectrum of vanadium ¶. The investigation of the spectrum of phosphorus was therefore undertaken with a view to separating the arc and various enhanced spectra from each other and to determining regularities and possibly series relationships in each. The present paper deals with the arc spectrum.

Experimental Procedure.

With the exception of possible lines in the infra-red, in which region no investigation has been made, the arc spectrum of phosphorus lies completely in the ultra-violet beginning at λ 2555.

The spectrum was produced in two ways: (1) by feeding phosphorus pentoxide into a carbon or a copper arc, and (2) by passing a discharge from an induction coil through a Geissler tube containing yellow phosphorus and hydrogen at a low pressure. The tube was provided with a quartz or fluorite window, and was used in the end-on position; the phosphorus was introduced through a side tube having a

* Communicated by Prof. A. Fowler, F.R.S.

† Geuter, *Zeit. Wiss. Phot.* v. p. 1 (1907).‡ De Gramont, *Comptes Rendus*, cxlvi. p. 1260 (1908).§ Paulson, *Ann. d. Phys.* xlv. p. 419 (1914).|| Foote & Mohler, *Phys. Rev.* xv. (1920).¶ Meggers, *Jour. Wash. Acad.* Aug. 1923; and Laporte, *Die Naturwissenschaften*, Sept. 1923.

ground-glass stopper. It was found unnecessary to heat the tube in order to bring out the phosphorus lines.

Four different spectrographs were employed for the various regions investigated:—

1. For wave-lengths greater than λ 2200, a quartz Littrow spectrograph giving a linear dispersion of 2.8 Å. to the millimetre at λ 2530.
2. For wave-lengths between λ 2200 and λ 2100, a Hilger quartz spectrograph having a linear dispersion of 4.7 Å. to the millimetre in that region.
3. For wave-lengths between λ 2100 and λ 1850, a Hilger quartz spectrograph having a linear dispersion of 12.3 Å. to the millimetre at λ 2030, and 9.4 Å. to the millimetre at λ 1890.
4. For wave-lengths shorter than λ 1850, a Hilger vacuum grating spectrograph giving an approximately normal spectrum in the first order with a linear depression of 17.2 Å. to the millimetre.

The wave-lengths of phosphorus lines greater than λ 1850 were measured on plates taken with an arc fed with phosphorus pentoxide as source.

Comparison Spectra.

The wave-lengths of the phosphorus lines are given in international angstroms reduced to vacuum, and for the various regions it was necessary to employ different comparison spectra.

Between λ 2550 and λ 2300 the iron arc was used for comparison, the wave-lengths being those given in Burns' tables. In this region the measurements are probably accurate to 0.05 Å.

In the region λ 2300 to λ 2100 the copper arc was used for comparison, the wave-lengths being those given by Hasbach*. The accuracy of the measurements in this region is probably as great as that of measurements between λ 2550 and λ 2300.

Between λ 2100 and λ 1850 a silver spark was employed, and the wave-lengths used were those given by Eder†. The possible error is about 0.05 Å. for lines in the region near λ 1850, and rather greater than that for lines near λ 2030.

The spectrograms taken with the vacuum spectrograph were treated as normal and the wave-lengths calculated from two known lines which appeared on the plate,

* Hasbach, *Zeitsch. Wiss. Phot.* p. 399 (1914).

† Eder, *Zeitsch. Wiss. Phot.* xiv. (1915).

namely a carbon line at $\lambda 1930\cdot61^*$ and a hydrogen line at $\lambda 1553\cdot3^\dagger$. The possible error in the values of these lines is about $0\cdot3 \text{ \AA}$.

Description of Spectra.

The arc spectrum of phosphorus from $\lambda 2550$ to $\lambda 1672$ probably consists of 35 lines, only four of which have been previously recorded. With the exception of the two faint lines $\lambda 1864\cdot1$ and $\lambda 1856\cdot6$, all the lines of wave-length greater than $\lambda 1850$ have been produced in two entirely different ways, thus establishing that they are due to phosphorus. They appear in the spectrum when P_2O_5 is added to a carbon or a copper arc, and also in the spectrum of a discharge through a tube containing yellow phosphorus and hydrogen at a low pressure. In the arc they are the only phosphorus lines which appear, but in the vacuum-tube discharge they may be the only phosphorus lines, or there may be others present as well, if the intensity of the discharge is great enough or the pressure of the hydrogen sufficiently low.

In the Schumann region an arc fed with a compound of phosphorus was found to be unsuitable as a source; consequently in this region the lines have been produced in only one way. Those which have been assigned to phosphorus are the additional lines which appear when yellow phosphorus is added to the tube. This assignment is probably correct, because in the region where two different sources could be used, the introduction of phosphorus into the vacuum tube was found to result only in extra lines due to phosphorus and none due to impurities. It must, however, be stated that the origin of lines of wave-lengths shorter than $\lambda 1850$ is not definitely established.

Although the line of shortest wave-length belonging to phosphorus that has been observed is $\lambda 1671\cdot5$, the plates in some cases showed lines of the hydrogen secondary spectrum down to $\lambda 1333$; but beyond $1671\cdot5$ no phosphorus lines could be observed among the strong groups of hydrogen lines. In order to determine to which spectrum of phosphorus the lines belonged, photographs were taken with different strengths of discharge, and the change in intensity of the lines observed. The lines which occur in the arc, can be produced alone of all the phosphorus lines by using an uncondensed discharge through phosphorus vapour in a vacuum tube containing also hydrogen at a comparatively high pressure, or by using a condensed discharge and hydrogen at a still higher pressure, so that H_α and H_β are

* Simeon, Proc. Roy. Soc. A, cii. (1922).

† Lyman, 'Spectroscopy of the Extreme Ultra-Violet,' p. 111.

very broad lines. When the pressure of the hydrogen is reduced and the intensity of the discharge through the phosphorus vapour is consequently increased, the arc lines become more intense at first and a few additional phosphorus lines make their appearance. With still further reduction of pressure of the hydrogen the arc lines decrease in intensity and become diffuse, while the new phosphorus lines brighten and very many more appear. Hence it is concluded that the lines which decrease in intensity in this manner belong to the arc spectrum, while the others are enhanced lines.

Table I. gives a list of the wave-lengths in international units reduced to vacuum, the wave-numbers in vacuum, the

TABLE I.

Wave-length.	Wave-number.	Intensity.	Character.	Source.
2555·68	39128·5	8	s*	Arc and vacuum tube.
2554·02	39154·0	9	s	" " "
2536·38	39426·3	10	s	" " "
2534·75	39451·6	8	s	" " "
2154·77	46408·7	7	s	" " "
2153·63	46433·2	6	s	" " "
2149·81	46515·7	8	s	" " "
2136·79	46799·2	8	s	" " "
2136·10	46814·2	6	s	" " "
2034·02	49163·7	7	s	" " "
2032·98	49188·9	6	s	" " "
2024·98	49383·2	6	s	" " "
2023·98	49407·6	7	s	" " "
1937·69	52419·4	1	s	" " "
1905·59	52477·2	0	s	" " "
1864·1	53645	1	s	Vacuum tube only.
1859·36	53782·0	6	s	Arc and vacuum tube.
1858·85	53796·7	8	s	" " "
1856·6	53862	0	d*	Vacuum tube only.
1851·11	54021·6	6	s	Arc and vacuum tube.
1846·8	54148	7	s	Vacuum tube only.
1844·0	54230	1	d	" " "
1834·5	54511	4	s	" " "
1825·9	54768	0·5	d	" " "
1820·3	54936	1	d	" " "
1787·5	55944	6·5	s	" " "
1782·7	56095	7	s	" " "
1774·8	56344	7	s	" " "
1719·0	58173	1·5	d	" " "
1693·8	59039	4·5	s	" " "
1689·1	59203	0·5	s	" " "
1685·8	59319	5	s	" " "
1679·5	59542	1·5	s	" " "
1674·4	59723	1·5	s	" " "
1671·5	59827	3	dv*	" " "

* s Means sharp.

d " diffuse.

dv " diffuse towards shorter wave-lengths.

intensities and character of the lines, and the sources in the spectrum of which the lines were observed. The intensities can be taken as having only local values, on account of the fact that many of the different groups of lines were either photographed on different plates, or on the same plate, the sensitiveness of which varied considerably within the range used.

Regularities in the Spectrum.

It will be seen that the spectrum consists of isolated groups of lines.

The group of four lines between $\lambda 2556$ and $\lambda 2535$ were found by De Gramont* to be the "raies ultimes" for phosphorus. For many elements the "raies ultimes" are the first lines of one of the series and also the lines corresponding to the radiation potential, which for phosphorus is $5.80 \pm .1$ volt†.

The extreme limits 5.70 volt and 5.90 volt of the radiation potential correspond to the spectral lines $\lambda 2165$ and $\lambda 2092$, which therefore do not agree with the wave-lengths of the "raies ultimes". But the group of five lines of wave-lengths $\lambda 2154.77$, $\lambda 2153.63$, $\lambda 2149.81$, $\lambda 2136.79$, $\lambda 2136.10$ in the phosphorus arc spectrum lie well within these limits, so that any one of them might be a resonance line. This group of lines is isolated, the interval between $\lambda 2154.77$ and the next line of longer wave-length being 380 A.U., and that between $\lambda 2136.10$ and the next line of shorter wave-length 102 A.U. The vapour of phosphorus is polyatomic at the temperature at which the radiation potential was measured, and in such a case it is not clear whether the radiation comes from excited molecules or from excited atoms which have previously been formed by dissociation of the molecule. If it comes from the former, the agreement of the resonance wave-length of phosphorus with that of a line in the arc spectrum is merely fortuitous. It is found, however, that in the case of hydrogen, which is diatomic, the first radiation potential, 10.2 volts, agrees with $\lambda 1215.7$, the first line of the Lyman series, and it is attributed by Horton and Davies‡ to atomic excitation. The case of phosphorus may be analogous.

The thirty-five lines recorded as belonging to the phosphorus arc spectrum are connected together by systems of

* De Gramont, *loc. cit.*

† Foote & Mohler, *loc. cit.*

‡ Horton & Davies, *Phil. Mag.* Nov. p. 873 (1923).

doublets of constant frequency differences, every one of the lines being involved. These are recorded in Table II. together with the intensities of the lines. It will be observed

TABLE II.

Wave-length.	Intensity.	Frequency difference.	Wave-length.	Intensity.	Frequency difference.
2555.68 } 2554.02 } 2536.38 } 2534.75 } 2154.77 } 2153.63 } 2034.02 } 2032.98 } 2024.98 } 2023.98 }	8 9 10 8 7 6 7 6 6 7	25.4 25.4 24.5 25.2 24.4	2154.77 * } 2024.98 * } 2153.63 * } 2023.98 * } 1774.8 } 1685.8 * }	7 6 6 7 7 5	2974.5 2974.4 2975
2149.81 } 2136.79 } 1856.6 } 1846.8 } 1844.0 } 1834.5 } 1693.8 } 1685.8 } 1679.5 } 1671.5 }	8 8 9 7 1 4 4.5 5 1.5 3	283.5 286 281 280 285	2555.68 * } 2154.77 * } 2554.02 * } 2153.63 * } 2149.81 * } 1858.85 }	8 7 9 6 8 8	7280.2 7279.2 7281.0
2534.75 * } 2136.79 * } 2153.63 * } 1859.36 } 2149.81 * } 1856.6 * } 2136.79 * } 1846.8 * } 1905.59 } 1671.5 * }	8 8 6 6 8 0 8 7 0 3	7347.6 7348.8 7346 7349 7350	2023.98 * } 1859.36 * } 1858.85 * } 1719.0 } 1820.3 } 1685.8 * }	7 6 8 1.5 1 5	4374.4 4376 4383
2555.68 * } 2536.38 * } 2554.02 * } 2534.75 * } 2149.81 * } 2136.10 }	8 10 9 8 8 6	297.8 297.6 298.6	2154.77 * } 2136.10 * } 1787.5 * } 1774.8 * } 1685.8 * } 1674.4 }	7 6 6.5 7 5 1.5	405.6 400 404
			1856.6 * } 1851.11 } 1825.9 * } 1820.3 * } 1693.8 * } 1689.1 }	0 6 0.5 1 4.5 0.5	160 168 164
			2136.10 * } 2034.02 * } 1907.69 } 1825.9 }	6 7 1 0.5	2349.4 2349
			1864.1 * } 1858.85 * } 1787.5 } 1782.7 }	1 8 6.5 7	152 151

* Used before.

that in some cases the frequency differences differ among themselves by several units, but in all cases they are within the limits of experimental error. In the Schumann region the possible error of measurement was estimated to be 0.3 Å., and at λ 1850 the corresponding possible error in the wave-number is 9 units and at λ 1671 it is 11 units. At λ 2556 a difference of 0.04 in the wave-length makes a difference of 0.6 in the wave-number. In spite of the variation between some of the frequency differences, it seemed worth while to record them, since the range of wave-number within which the lines lie is comparatively great for so small a number of lines, and the approximate agreement is more significant than if the lines were close together. They serve, at any rate, to show that the arc spectrum of phosphorus almost certainly consists of doublets, and thus falls into line with elements obeying the Sommerfeld-Kossel displacement law, which requires the arc spectrum of phosphorus to contain series of doublets.

The frequencies of all the lines up to λ 1858.85, with the exception of the three lines λ 1907.69, λ 1905.59, λ 1864.1, which are of low intensity, can be expressed by means of nine terms. These lines are among those which are known definitely to belong to the arc spectrum of phosphorus, and if the terms are a , b , c , d , e , and α , β , γ , δ , the lines are as follows:—

TABLE III.

λ 2555.68 (8) $a-\alpha$	λ 2136.10 (6) $\gamma-b$
λ 2554.02 (9) $\beta-a$	λ 2034.02 (7) $a-d$
λ 2536.38 (10) $a-b$	λ 2032.98 (6) $\beta-d$
λ 2534.75 (8) $\beta-b$	λ 2024.98 (6) $a-e$
λ 2154.77 (7) $a-c$	λ 2023.98 (7) $\beta-e$
λ 2153.63 (6) $\beta-c$	λ 1859.36 (6) $\delta-c$
λ 2149.31 (8) $\gamma-a$	λ 1858.85 (8) $\gamma-c$
λ 2136.79 (8) $\delta-b$	

Some of these terms can be identified by arranging the lines in multidoublets, similar to those discovered by Catalán* in the arc spectrum of scandium.

The group at about λ 2550 can be arranged as a multidoublet of the PP' type with the expected relative intensities as follows:—

* Catalán, *Anal. d. Soc. Esp. Fis. y Quim.* xx, p. 606 (1922).

λ .	ν .	Intensity.	Designation.
2555.68	39128.5	8	$P_1' P_2$
2554.02	39154.0	9	$P_2' P_2$
2536.38	39426.0	10	$P_1' P_1$
2534.75	39451.6	8	$P_2' P_1$

The scheme of the multidouplet is

(8)		(9)
39451.6	297.6	39154.0
25.4		25.4
(10)		(8)
39426.3	297.8	39128.5.

Hence $P_2 - P_1 = 297.7$ and $a = P_2$, $b = P_1$; also $P_2' - P_1' = 25.4$ and $\beta = P_2'$, $\alpha = P_1'$. The former separation occurs once more and the latter three times more.

If the lines are correctly represented in Table III., there is a multidouplet of the DP type among the $\lambda 2140$ group as follows :—

λ .	ν .	Intensity.	Designation.
2149.81	46515.7	8	$D_2 P_2$
2136.79	46799.2	8	$D_1 P_1$
2136.10	46814.2	6	$D_2 P_1$

(6)		(8)
46814.2	293.5	46515.7
15.0		
(8)		
46799.2		

Hence $D_2 - D_1 = 15.0$ and $\gamma = D_2$, $\delta = D_1$. The separation 15.0 occurs once again at $\lambda 1858$. The group of four lines near $\lambda 2030$ is very like a multidouplet of the PP' type, except that the intensities are in the opposite order

to that expected. It can be represented as follows if $P_1'' > P_2''$:—

λ .	ν .	Intensity.	Designation.
2034.02	49163.7	7	$P_1' P_1''$
2032.98	49188.9	6	$P_2' P_1''$
2024.98	49383.2	6	$P_1' P_2''$
2023.98	49407.6	7	$P_2' P_2''$

(7)		(6)
49407.6	218.7	49188.9
24.4		25.2
(6)		(7)
49383.2	219.5	49163.7

Hence $P_1'' - P_2'' = 219.1$ and $d = P_1''$, $e = P_2''$. The remaining four lines in Table III. have only one term, common to them all, which is not identified. This classification of the lines is not completely satisfactory, but it tends to confirm the doublet nature of the series to be expected in the arc spectrum of phosphorus.

Summary.

1. The arc spectrum of phosphorus has been investigated from the visible region up to λ 1671. The whole spectrum lies in the ultra-violet beyond λ 2555, and probably consists of thirty-five lines within this range.

2. A group of five close lines, which is widely separated from neighbours, has been found such that any one of the lines agrees in wave-length with that calculated from the radiation potential.

3. The frequencies of all the lines are connected by systems of doublets of constant frequency differences, and thus the arc spectrum of phosphorus probably obeys the Sommerfeld-Kossel displacement law.

4. The frequencies of fifteen of the strongest lines can be expressed by means of nine terms, and some of these lines can be arranged as multidoublets.

The work described in this paper has been carried out under the direction of Professor A. Fowler, and the author wishes to express her gratitude to him for his generous help and interest.

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LXXXVII. *The Rate of Heat Transmission from the Working Fluid in an Internal Combustion Engine.* By Prof. A. H. GIBSON, D.Sc.*

1. **T**HE rate of heat transmission from the hot gases contained in a metal chamber to the cool walls depends upon the temperature difference, the density, the turbulence, and to some extent on the dimensions of the chamber.

In experiments on cooling following explosion in an explosion vessel the turbulence is small, and heat transmission is mainly due to radiation. Under these conditions, experiments by Sir Dugald Clerk † indicate that the rate of heat transmission is proportional to ϕ^n , where ϕ is the temperature difference, and where, between the limits of 1100°C. and 1450°C. , n has a mean value of $2\cdot8$. Hopkinson's results ‡ between 1300°C. and 1760°C. show $n=2\cdot45$, and Petavel's § experiments between 320°C. and 2200°C. show $n=2\cdot35$. In the experiments of Clerk and Hopkinson the density was atmospheric. In those of Petavel it was considerably higher (up to 75 atmospheres). Petavel's experiments at different densities indicate that the heat transmission is proportional to ρ^n at a given temperature, where $n=0\cdot35$ at 1760°C. Bairstow and Alexander's || experiments at densities from 1 to 3 atmospheres indicate a value of $n=0\cdot35$ at 1400°C. , but this value is appreciably reduced at higher temperatures.

On the other hand, when, as in an engine in operation, the transference of heat from the gas to the metal surfaces is largely dependent on the velocity of the gas, the heat-loss is more nearly proportional to the density. Thus in his gas-engine experiments Hopkinson ¶ found that the total heat-loss, including that after release, was proportional to ρ^9 , while from piston temperature measurements he found it proportional to ρ^{73} .

2. A knowledge of the rate of heat transmission under the conditions holding during the working cycle of an internal combustion engine would be of great value in enabling the rate of heat-flow into the exposed surfaces and the magnitude of the surface fluctuations of temperature to be determined.

* Communicated by the Author.

† Clerk, 'The Petrol and Gas Engine,' vol. i. p. 204 (1909).

‡ Proc. Roy. Soc. A, 1906, p. 387.

§ Clerk, 'The Petrol and Gas Engine,' vol. i. p. 166.

|| Proc. Roy. Soc. A, 1905.

¶ Proc. Inst. C. E. clxxvi. pt. ii. (1908-9)

Its direct experimental determination is one of much difficulty, and no definite values have hitherto been available, especially at the temperatures and with the degrees of turbulence which obtains in a high-speed petrol engine in operation. Some idea of its magnitude may be deduced from the valuable data obtained by Sir Dugald Clerk * in his experiments on the cooling of the fluid in the cylinder of a gas-engine. These measurements, however, refer not to the working stroke, but to the succeeding strokes, in which the turbulence is less by some unknown amount than in the normal working stroke.

Its value under operating conditions may be deduced indirectly (*a*) from measurements of the temperature gradient along a radius of the piston of the engine, or (*b*) from measurements of the cyclical fluctuation of surface temperature of the piston or walls of the combustion chamber; and the present paper is devoted to an examination of such measurements with a view of obtaining a reasonably close approximation to this value.

3. Some few measurements of piston temperatures in the cylinders of gas-engines are available, notably by Hopkinson on a cast-iron piston 11.5 in. diameter by 1.5 in. thick, at 180 revs. per minute; by Coker and Scoble † on a cast-iron piston 7 in. diameter by $\frac{3}{8}$ in. thick, at 200 and 240 revs. per minute; and by Jardine and Jehle ‡ on two aluminium pistons, 5 in. diameter and respectively $\frac{1}{4}$ in. and $\frac{3}{8}$ in. thick, in a petrol-engine cylinder at 800 r.p.m. In addition to these, the author has carried out experiments on a number of aluminium and cast-iron pistons of various thicknesses, 100 mm. diameter, in a petrol-engine cylinder at speeds of 1800 and 2000 r.p.m. § The data thus cover a wide range of operating conditions.

The amount of available data regarding the magnitude of the fluctuations of surface temperature is not large. A number of experimental determinations are, however, given in the paper by Messrs. Coker and Scoble ||, and these have been used as a check on the values obtained from the piston temperature measurements.

4. If the temperature gradient across the face of a piston is known, the rate of reception of heat "*h*" per unit area of the face, or rather the difference between the rate at which

* Proc. Roy. Soc. A, lxxvii. p. 499 (1906).

† Proc. Inst. C. E. cxcvi. pt. ii. (1913-14).

‡ American Society of Automotive Engineers (May 1921).

§ Advisory Committee for Aeronautics. L.A.S.C. Reports, No. 13 (May 1918).

|| *Loc. cit.*

heat is being received by the working face and dissipated at the lower face of the piston crown, is given very approximately by

$$h = \frac{4kt\theta}{a^2 + t^2}, \quad \dots \quad (1)$$

where θ is the difference of temperature between the centre and a point at radius a ,
 t is the thickness of the piston crown,
 k is the conductivity of the material,

If $(\theta_1 - \theta_2)$ be the difference of temperature at two radii a_1 and a_2 , this becomes

$$h = \frac{4kt(\theta_1 - \theta_2)}{(a_2^2 - a_1^2)}. \quad \dots \quad (2)$$

In a piston in which the thickness of the crown varies with the radius, if over any portion of the crown between radii a_1 and a_2 the thickness is proportional to the radius so that $t = Ca$, we have

$$\begin{aligned} \delta\theta &= \frac{h(a_2^2 - a_1^2)}{4kt}, \\ &= h \times \frac{2a\delta a}{4kt}, \\ &= h \frac{\delta a}{2kC}; \\ \therefore \theta_1 - \theta_2 &= \frac{h}{2kC} \int_{a_1}^{a_2} da, \\ &= \frac{h(a_2 - a_1)}{2kC}. \quad \dots \quad (3) \end{aligned}$$

In a number of the author's pistons (viz. A, A', B, and C, Table I.) this condition is satisfied over the range of radii 0.5 in. to 1.0 in. (1.27 cm. to 2.54 cm.), the value of C being 0.31.

5. *Cyclical Fluctuations of Surface Temperature.*—On the assumptions that the working fluid in contact with the metal has a cyclical fluctuation of temperature of $\pm A^\circ \text{C}$.; that the heat transmission from the gas to the metal is directly proportional to their difference of temperature; and that this produces a simple harmonic fluctuation of temperature in the metal: it may be shown that in the case

of a large flat surface the magnitude "a" of the fluctuation of surface temperature is given by

$$a = \frac{Ae'}{\sqrt{\pi n \rho s k + (e' + \sqrt{\pi n \rho s k})^2}}, \quad \dots \quad (4)$$

where n is the number of explosions per second,

ρ is the density of the metal,

s is the specific heat of the metal,

k is the thermal conductivity of the metal,

e' is the receptivity, *i. e.* the heat transmitted from the gas to the surface per second per unit area per degree difference of temperature between metal and gas.

If e' is relatively small, as is shown later to be the case,

$$a = \frac{Ae'}{\sqrt{2\pi n \rho s k}} \text{ approximately. } \dots \quad (5)$$

So that

$$\frac{a}{A} \propto \frac{1}{\sqrt{n}} \text{ for a piston of given material,}$$

$$\frac{a}{A} \propto \frac{1}{\sqrt{\rho s k}} \text{ for pistons of different materials operating at the same speeds of rotation.}$$

The assumption that e' in the above formulæ is a constant is, however, very far from being true. Actually, Sir Dugald Clerk's experimental results indicate that under the conditions obtaining in a gas-engine, the heat transmission " h " per unit area per second is more nearly proportional to ϕ^n , where ϕ is the difference of temperature between gas and metal, and where n is very nearly equal to 2*. If n be assumed equal to 2 for convenience in calculation, the results will be very much nearer representing the true state of affairs than those deduced on the assumption that $n=1$, and if $n=2$ it may be shown that the formula corresponding to (5) is

$$a = \frac{e\{(T_1 - \theta_0)^2 - (T_2 - \theta_0)^2\}}{2\sqrt{2\pi n \rho s k}}, \quad \dots \quad (6)$$

where T_1 is the maximum temperature of the gas during the cycle,

T_2 is the minimum temperature of the gas during the cycle,

θ_0 is the mean temperature of the surface during cycle,

$e\phi^2 = h$ = heat transmitted per unit area per second from gas to surface.

* See Section 9.

6. The essential data from the author's pistons, under full-load conditions, are given in Table I.

TABLE I.

Line.	Piston.	Temperature ° C. at					Mean wall temp. ° C.
		Centre.	·5 in. rad.	1·0 in. rad.	1·5 in. rad.	Edge.	
1 ...	A	194°	197°	167°	149°	139°	112°
2 ...	A'	235	240	210	187	175	119
3 ...	B	198	199	169	152	140	114
4 ...	C	205	210	183	160	147	122
5 ...	G	215	229	201	170	148	120
6 ...	Cast iron ..	409	419	366	283	184	120

An examination of the drawings of the aluminium pistons shows that at the radius 1·5 in. the effect of the large fillet joining the crown to the skirt has an appreciable effect on increasing the thickness. Over the range of radii from 0·5 in. to 1·0 in., however, the thickness is constant in piston G, while in pistons A, A', B, and C it is sensibly proportional to the radius. Taking the average value of the gradient over this range of radius in these four pistons, calculations based on equation (3) give $h=5·56$ C.G.S. units, while for piston G, $h=5·75$ C.G.S. units. The corresponding value of h for the cast-iron piston is 1·60. The values of h deduced from these experiments and from those by other observers are given in Table II.

TABLE II.

Authority.	Type of Engine.	h (C.G.S. units.)	e (C.G.S. units.)
HOPKINSON ...	Gas-engine: 11·5 in. C.I. piston; 180 r.p.m.; stroke 21 in. (Normal mixtures).....	1·43	$3·9 \times 10^{-6}$
COKER	Gas - engine: 7 in. C.I. piston; 200 r.p.m.; stroke 15 in. (Normal mixtures).....	1·16	$3·4 \times 10^{-6}$
JARDINE & JEHLE.	Aero-engine: 5 in. aluminium piston; 800 r.p.m; stroke 7 in. Piston ·25 in. thick.....	4·15	$9·0 \times 10^{-6}$
	„ ·375 in. „	4·05	$8·8 \times 10^{-6}$
AUTHOR	Petrol-engine: 1800 r.p.m; stroke 140 mm. Aluminium pistons A, A', B, C, 100 mm. diam.	mean 5·56	$11·0 \times 10^{-6}$
	Aluminium piston G, 100 mm. diam.....	5·75	$11·0 \times 10^{-6}$
	Cast - iron piston, 100 mm. diam.	1·60	$5·1 \times 10^{-6}$

In calculating these values, k has been taken as 0.11 for cast iron at 200° C., 0.102 at 350° C.; 0.38 for aluminium alloy at 200° C. and 0.39 at 300° C.*

The value of h deduced from equations (1), (2), or (3) represents the mean rate of heat inflow during the cycle, and the determination of e from h necessitates a knowledge of the mean square of the temperature difference between gas and surface on a time base during the cycle.

On the usual assumption that the fluctuation of gas temperature is simple harmonic, it may be shown that this mean square is equal to †

$$\left\{ \frac{T_1 - T_2}{2} - \theta_0 \right\}^2 + \frac{\{T_1 - T_2\}^2}{8} \dots \dots (9)$$

Calling this ϕ^2 , we then have $h = e\phi^2$. An examination of Coker's measurements of gas temperature throughout the cycle shows, however, that the assumption as to simple harmonic fluctuation gives results which are very far from the truth. Thus, taking the difference of temperature between gas and piston at crank angles of 30°, 90°, etc. in test G ‡ of Coker's paper, and calculating the mean of the squares of the differences throughout the cycle gives 335,000. In this test $T_1 = 2040^\circ$ C. approx.; $T_2 = 217^\circ$; and the mean temperature θ_0 of the piston between the points of measurement is 196°. Inserting these values in equation (7) makes ϕ^2 equal to 1,291,000, or 3.85 times its true value as deduced from the temperature curve. A similar examination of all the test results in this latter paper shows that this ratio varies between 3.85 and 4.09 in the different experiments, the maximum variation from the value 4.0 being less than 4 per cent. It is probable, therefore, that without serious error it may be assumed that under normal conditions of operation in such engines the value of ϕ^2 is given by

$$\frac{1}{4} \left\{ \left(\frac{T_1 + T_2}{2} - \theta_0 \right)^2 + \frac{(T_1 - T_2)^2}{8} \right\},$$

and that e equals h divided by this expression.

In Coker's full-load tests the following are the approximate values of the temperatures: $T = 2120^\circ$ C., $T_2 = 270^\circ$, $\theta_0 = 230^\circ$; while the value of h , deduced from the mean temperature across the piston, is 1.16 C.G.S. units. The

* These values were measured for the materials from which the 100-mm. pistons were made.

† See Appendix.

‡ Proc. Inst. C. E. pt. ii, p. 42 (1913-14).

mean value of ϕ^2 is 340,000, making the mean value of $e = 3.41 \times 10^{-6}$.

In Hopkinson's experiments the compression ratio was higher than in those of Coker, being 6.37 as compared with 5.8, and T_1 would be approximately 2350°C . The mean piston temperature was 350°C .; and assuming $T = 300^\circ \text{C}$.

$$\begin{aligned}\phi^2 &= \frac{1}{4} \left\{ \left(\frac{2650}{2} - 350 \right)^2 + \left(\frac{2050}{8} \right)^2 \right\}, \\ &= 369,000.\end{aligned}$$

The mean value of h deduced from the temperature gradients across the piston is 1.43, making $e = 3.87 \times 10^{-6}$, a value 13 per cent. greater than that deduced from Coker's experiments. The difference is probably partly due to the greater density of the charge and partly a dimensional effect due to the relatively greater radiation per unit area at a given temperature from a large than from a small body of gas. Allowing for this, the two sets of results appear to be in close agreement.

Comparing these values with those deduced from Clerk's experiments on a gas-engine cylinder*, it appears that they are approximately 35 per cent. higher. This is to be accounted for by the fact that in Clerk's experiments the measurements were made over a number of successive expansion and compression strokes during which the turbulence would be appreciably less than on the stroke following admission of gas to the cylinder.

In the petrol-engine tests the compression ratio was varied from 4.6 to 5.3. The results showed that the piston-temperature gradient is only very slightly affected by the degree of compression, but that it is slightly less with the higher compression ratios. In these tests the maximum temperature of the working fluid can only be assumed; but it is certainly higher than in the gas-engine tests, and is probably in the neighbourhood of 2400°C ., except in the case of the author's tests on a cast-iron piston, where, on account of the richer mixture necessary for satisfactory operation, it would probably be about 2300°C . The minimum temperature of the working fluid has been taken at 250°C . In each of these cases the mean temperature of the piston between the points of measurement is known, and making the foregoing assumptions as to gas temperatures, the values of e become as shown in Table II.

* Section 9.

From these figures it appears that the values obtained for the various aluminium pistons are also in reasonable agreement, the difference between the mean value 8.9×10^{-6} deduced from Jardine and Jehle's tests at 800 r.p.m. and the author's mean value of 11.0×10^{-6} at 1800 r.p.m. being explained by the greater turbulence of the working fluid at the higher speeds of rotation. It will be noted that the latter value of e is three times as great as that obtained in the gas-engine tests, a difference which is also probably due mainly to the difference in turbulence.

The value of e deduced for the cast-iron piston in the author's experiments is, however, much lower than that found for the aluminium pistons. It is, in fact, only about one-half of the latter value. No complete explanation of this discrepancy can be put forward at the moment. It is probably partly due to the greater cooling effect of oil-splash on the under side of this hot piston, but mainly to carbon deposits on the piston crown.

7. Adopting the value 3.41×10^{-6} deduced from Coker's piston temperature-gradient measurements*, and using this in equation (6),

$$a = \frac{e\{(T_1 - \theta_0)^2 - (T_2 - \theta_0)^2\}}{2\sqrt{2\pi n\rho sk}},$$

the value of " a ," the semi-amplitude of the fluctuations of surface temperature, may be deduced, and this may be compared with experimental measurements of the fluctuation.

Adopting the same mean values as before, viz. $T_1 = 212^\circ$, $T_2 = 270$, $\theta_0 = 230^\circ$, and taking for a cast-iron piston $\rho = 7.8$, $s = 0.11$, $k = 0.11$, n (at 200 r.p.m.) $= \frac{100}{60}$; this makes

$$a = \frac{3.41 \times 3.57}{2} = 6^\circ.1,$$

indicating a total fluctuation of $12^\circ.2$ C.

The measured fluctuations of temperature at a depth of 0.02 in. (0.51 cm.) obtained from the tables given in the paper have a mean value of 29° C. It may readily be shown that the fluctuation of temperature at any depth x is proportional to

$$e^{-\sqrt{\frac{\pi n \rho s}{k}} \cdot x} \quad \dagger,$$

so that for cast iron at 100 cycles per minute the corresponding surface fluctuation would be 40° C., which is much higher than the value ($12^\circ.2$ C.) calculated. It was however

* Proc. Inst. C. E. vol. cxvii. pt. ii. (1913-14).

† Here e is the base of the Napierian logarithms.

pointed out in the discussion on the paper that there is reason for thinking that the measured values may have been greater than the true cyclical fluctuation, and in earlier tests on the same engine a measured fluctuation of temperature of $7^{\circ}\cdot 2$ C. was obtained at 240 r.p.m. at a depth of $\cdot 015$ in. in the metal of the combustion space, corresponding to a surface fluctuation of $9^{\circ}\cdot 3$ C., which would be equivalent to a fluctuation of $10^{\circ}\cdot 2$ C. at 200 r.p.m.

8. Measurements of the fluctuation of temperature at the centre of the head of the inlet valve and of the exhaust valve of the same engine at a depth of $\cdot 02$ in. at 200 r.p.m. gave mean values of 15° C. and 12° C. respectively, corresponding to surface fluctuations of $20^{\circ}\cdot 7$ and $16^{\circ}\cdot 5$. The mean temperature of the inlet valve was 250° C. and of the exhaust valve 370° C. Taking $T_1=2120^{\circ}$ C., T_2 for the exhaust valve $=320^{\circ}$ C., and T_2 for the inlet valve $=100^{\circ}$ C. owing to the influx of cold mixture during the suction stroke, this makes $e=5\cdot 90 \times 10^{-6}$ for the inlet valve and $e=5\cdot 43 \times 10^{-6}$ for the exhaust valve. These values are 70 per cent. greater than those deduced from the piston—a difference which is to be expected owing to the velocity of flow over these valve surfaces during the inlet and exhaust strokes.

9. Clerk's experiments on the rate of cooling of the gases in the cylinder of a gas engine during repeated expansions and compressions after explosion * are valuable as indicating the effect of temperature on the interchanges of heat under these conditions. The experiments on this engine, which has a bore of 14 in. and a stroke of 22 in., were carried out at 160 r.p.m. The compression ratio was 6:1, so that the density during the period of heat transmission ranged from 1 to 6 approximately. Taking the mean temperature throughout a complete stroke, Clerk gives the following values (line 2) for the heat-loss per second per sq. ft., based on the area exposed when the piston is full out †:—

Mean temperature, ° C.	1400°	1300°	1150°
Heat-loss in cub. foot, degrees per sec.	400	340	260
$k + (T_0 - \theta_0)^2$	$1\cdot 63 \times 10^{-11}$	$1\cdot 66 \times 10^{-11}$	$1\cdot 68 \times 10^{-11}$
$e \times 10^6$	2\cdot 28	2\cdot 30	2\cdot 31

In these experiments the mean temperature of the cooling surfaces was 190° C. Converting the heat-loss into C.G.S. units, and dividing by $(T_0 - \theta_0)^2$, where T_0 is the mean gas temperature, gives the values shown in line 3 of the above table. From the data given in the original paper it is

* Proc. Roy. Soc. A, lxxvii. p. 499 (1906).

† Clerk, 'The Gas, Petrol, and Oil Engine,' vol. i. p. 230 (1909).

possible to determine the approximate values of T_1 and T_2 in each case, and so to get the mean square of the temperature difference as defined in expression (7). Making this correction, and assuming that the mean exposed area during the stroke is that exposed at half-stroke, the new values for e ($=h/\phi^2$) become as shown in line 4. These values are of the same order, but about 35 per cent. less than the values obtained in the experiments of Coker and Hopkinson; and when due weight is given to the difference in the conditions as regards turbulence in the two sets of experiments, the agreement would appear to be satisfactory.

10. The foregoing results indicate that the value of e to be used in calculations of the probable heat-flow at any point of a given piston by the use of formula (1), (2), or (3), depends largely on the turbulence of the working fluid. At the compression ratios usual in practice, and under normal working conditions, it ranges from about 3.6×10^{-6} in a slow-speed gas-engine at 200 r.p.m. to 11.0×10^{-6} in a high-speed petrol-engine at 1800 r.p.m.

Adopting these values, it is of interest to calculate the probable fluctuations of surface temperature.

In a petrol-engine making 1800 r.p.m. having an aluminium piston, $n=15$, $\rho=2.9$, $s=0.21$, $k=.38$, and the value of $\pi n \rho s k$ in C.G.S. units is 11.0, a value which is large compared with e .

Under these conditions

$$a = \frac{e\{(T_1 - \theta_0)^2 - (T_2 - \theta_0)^2\}}{2 \sqrt{2\pi n \rho s k}},$$

and assuming $T_1=2400^\circ \text{C.}$, $T_2=250^\circ \text{C.}$, $\theta_0=250^\circ \text{C.}$, this makes

$$a = \frac{11.0 \times 4.63}{9.4} = 5.5^\circ \text{C.},$$

or a total surface fluctuation of 11.0°C.

For a cast-iron piston, $\rho=7.8$, $s=0.11$, $k=0.11$, and adopting the same values for e , T_1 , and T_2 , but assuming $\theta_0=400^\circ \text{C.}$,

$$a = \frac{11.0 \times 4.65}{6.23} = 8.2^\circ \text{C.},$$

or a total fluctuation of 16.4°C.

From these figures it is apparent that, even making allowance for a considerable error in the value of e , the fluctuation of surface temperature at such speeds is negligible.

11. *Experimental Verification.*—The difficulty of experimentally measuring the surface fluctuation in an engine at

very high speeds is almost insuperable, and to avoid this the author carried out a series of experiments * which, though not directly representing the conditions obtaining in the metal of the piston of an engine, approximate to these.

The experiments were carried out on a series of bars of aluminium-copper-zinc alloy, having a composition of Al, 92 per cent.; Cu, 7 per cent.; Zn, 1 per cent. The eutectic melting-point of this alloy was carefully measured, and found to be 540°C . The bars are $\frac{5}{8}$ in. diameter and 6 in. long. One end of each bar was turned down to $\frac{1}{2}$ in. diameter for a length of $\frac{1}{8}$ in., and an asbestos washer 3 in. diameter was fitted against the shoulder thus formed. A Pt Ir thermocouple was plugged into the bar at a point $\frac{3}{16}$ in. from this end. The bar was clamped horizontally.

A sheet-steel sliding shutter having a central $\frac{1}{2}$ in. square hole was operated by an electric motor, and made 450 reciprocations per minute immediately in front of the turned end of the bar. When the shutter is in the middle of its travel, the blast from a blowpipe (flame temperature approximately 1650°) impinges directly through the hole in the shutter on to the turned end of the bar. Owing to the motion of the shutter, the end of the bar is thus subjected to an intense heat 900 times per minute. The total period during which the flame is in contact with the bar is approximately one-fourth of each cycle. The conditions thus approximate fairly well to those obtaining in the metal of an aero-engine making 1800 revs. per minute. Each experiment lasted for 50 minutes, after which the bar was cut in two along the axis and was polished, etched, and examined microscopically.

In carrying out a test the blowpipe was turned full on. The temperature of the thermocouple was then observed until it became steady. This temperature was generally about 350°C . A bunsen burner was then placed under the further end of the bar, and was adjusted until the thermocouple gave steady readings at the desired temperature.

The following table shows the results of the tests:—

Bar No.	Temperature at thermocouple.	Results of micro. examination.
1.	526°C	No change in structure.
2.	536°C	" "
3.	550°C	Eutectic segregated over whole mass of bar up to 1 inch from heated face. No apparent difference between heated face and interior of bar near face.

* Advisory Committee for Aeronautics. L.A.S.C. Reports, No. 13, p. 18 (May 1918).

The fact that no segregation of the eutectic even at the exposed and heated face was observed when the mean temperature at a point $\frac{1}{16}$ in. deep was as high as 536°C . indicates that the fluctuation of surface temperature must have been appreciably less than 4°C . Calculations based on the known gas temperatures, using formula (6), show that this should be approximately $1^{\circ}\cdot 5^{\circ}\text{C}$.

12. *Conclusions.*—The investigations would point to the following conclusions:—

(1) Assuming that the heat transference from a hot gas to a metal surface per second per unit area equals $e\phi^2$, where ϕ is the difference of temperature in degrees centigrade, the mean rate of heat transmission throughout the cycle under the conditions obtaining under normal conditions of operation in engines having compact cylindrical combustion chambers with compression ratios between 4·5 and 6·5 is very approximately equal to

$$e \times 25 \left[\left\{ \frac{T_1 - T_2}{2} - \theta_0 \right\}^2 + \frac{(T_1 - T_2)^2}{8} \right],$$

where T_1 and T_2 are the maximum and minimum gas temperatures and θ_0 is the mean temperature of the metal surface.

For the piston and combustion head surfaces, e has a value which varies from about $3\cdot 6 \times 10^{-6}$ in gas-engines of 6 to 12 in. diameter at speeds in the neighbourhood of 200 r.p.m. to $11\cdot 0 \times 10^{-6}$ in high-speed petrol-engines at about 2000 r.p.m. These values are in C.G.S. units. The corresponding values expressed in C.H.U. per sq. ft. per minute are $4\cdot 4 \times 10^{-4}$ and $13\cdot 5 \times 10^{-4}$.

(2) The semi-amplitude of the cyclical fluctuation of surface temperature on the same assumptions is given by

$$a = \frac{e[(T_1 - \theta_0)^2 - (T_2 - \theta_0)^2]}{2\sqrt{2\pi n p s k}}.$$

Owing to the velocity of flow over their surfaces, the values of e to be adopted in calculations of the fluctuation of temperature in exhaust or inlet valves are approximately 70 per cent. greater than those given above.

(3) In a high-speed petrol-engine at 2000 r.p.m. the fluctuation of temperature in the surface of the piston, if of aluminium, is of the order $\pm 5^{\circ}\text{C}$.

(4) In conclusion the author would emphasize the fact that owing to the comparatively limited amount of available data, and the assumptions which have had to be made regarding the temperatures of the working fluid, the foregoing values for e can only be considered as approximate. In spite of the difference in the methods by which they have been deduced, they do however show a satisfactorily close agreement; and it is hoped that the accumulation of data on these or other lines will enable more close accurate values to be deduced in due course.

APPENDIX.

Let T_1 be the maximum temperature of the gas,

T_2 „ minimum „ „

T_0 „ mean „ „

θ_0 be the temperature of the surface (supposed constant),

$h = e(T - \theta_0)^2 =$ heat transmitted from gas to surface
per second per unit area,

$n =$ no. of cycles per second.

Then heat transmitted per sq. cm. per cycle

$$\begin{aligned} &= \frac{2e}{2\pi n} \int_{\pi/2}^{3\pi/2} \left\{ T_0 - \theta_0 + \left(\frac{T_1 - T_2}{2} \right) \sin \theta \right\}^2 d\theta, \\ &= \frac{e}{n} \left\{ (T_0 - \theta_0)^2 + \frac{(T_1 - T_2)^2}{8} \right\}, \\ &= \frac{e}{n} \left\{ \left(\frac{(T_1 + T_2)}{2} - \theta_0 \right)^2 + \frac{(T_1 - T_2)^2}{8} \right\}. \end{aligned}$$

Mean heat inflow per sec. per sq. cm.

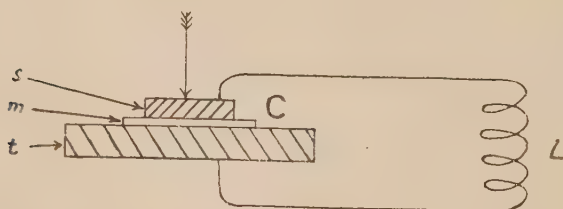
$$= e \left\{ \left(\frac{(T_1 + T_2)}{2} - \theta_0 \right)^2 + \frac{(T_1 - T_2)^2}{8} \right\}.$$

LXXXVIII. *A Valve Method of Detecting Minute Slipping in Metals.* By CECIL HANDFORD, M.Met.

[Plate VI.]

1. IT was required in the course of an investigation on the fatigue of metals to determine the stress which produced the first minute slips in a specimen under tension, that is, the point at which the elastic limit of the metal was locally exceeded in one or more crystal grains. For this purpose a polished surface was examined while the specimen was under stress, in order to observe the first appearance of the well-known slip-bands. This method proved to be insufficiently sensitive, no slip-bands being visible under a low or high magnification until the actual amount of slip was considerable. As a rule the faint ruffling of the surface could be perceived by the unaided eye, under proper condition of illumination, as soon as by means of the microscope, and this in spite of very numerous experiments in the direction of more suitable methods of illumination. A method depending on the alteration of capacity of a condenser, and making use of thermionic valves, was therefore tried. This method was suggested by the description of Professor Whiddington's valve Ultra-micrometer, given to the Wireless Society of London, December 21st, 1920. His arrangement was modified in accordance with the following description, to suit it to the problem in hand and the laboratory conditions prevailing.

Fig. 1.

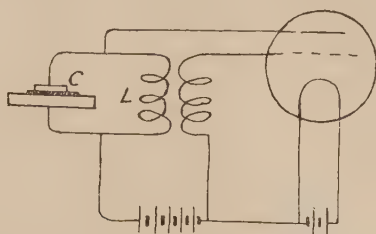


2. A piece of metal, *s*, having one face accurately levelled and polished, is held by spring pressure against the levelled and polished surface of the test-piece, *t*, but separated from it by a very thin plate of mica, *m*. This forms a condenser, *C*, across which is joined an inductance, *L*, forming an oscillatory circuit (fig. 1). This circuit is connected to a

* Communicated by Professor C. H. Desch, F.R.S.

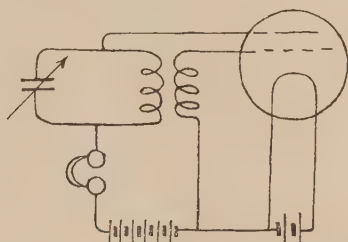
three-electrode thermionic valve so as to oscillate at its natural frequency (fig. 2).

Fig. 2.



A second similar circuit is formed having a small variable condenser instead of the one formed on the surface of the test-piece, and is adjusted so as to oscillate at a slightly lower frequency (fig. 3). Included in this second valve circuit is a pair of telephones.

Fig. 3.



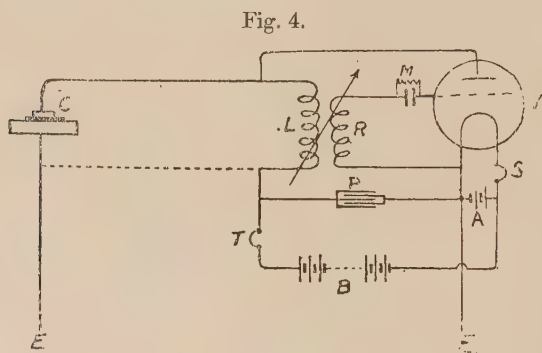
Let the two frequencies of oscillation be f_2 and f_1 respectively. The two circuits are coupled together so that the oscillations of the first circuit are impressed on the second. There will then be beats of amplitude of oscillation in the second circuit, occurring at the rate of $f_2 - f_1$ per second. These beats on rectification will give a musical note of frequency $f_2 - f_1$ in the telephones.

If the surface of the test-piece becomes distorted in any way, the small auxiliary plate will be pushed away and the average distance between the two surfaces increased. The resultant decrease in capacity of the condenser which they form will raise the frequency of the first oscillatory circuit to, say, f_3 .

The beat-note appreciated in the telephones will now be $f_3 - f_1$, a higher note. Thus, under these conditions, a rise in note in the telephones indicates distortion of the test-piece surface.

The method is sensitive because the frequency of the first circuit varies inversely with the capacity of its condenser, while the indication given in the telephones is its arithmetical change. Hence, by making the oscillation frequency very high and the datum beat-note in the telephones very low, large changes of pitch are obtained for very small variations in the capacity of the condenser. After experiment an oscillation frequency of 10 million was decided on, as being the highest that could be generated and handled easily.

3. The actual apparatus used consisted of two units, the "Transmitter," whose condenser is made up of the test-piece and auxiliary plate, and the "Receiver" containing the telephones. The complete circuit diagram of the Transmitter is shown in fig. 4.



Circuit diagram of "Transmitter."

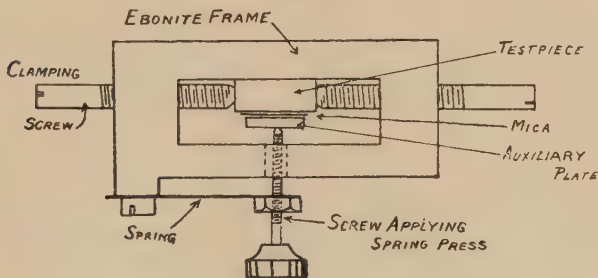
The inductance, L , of the oscillatory circuit consists of a spiral winding of $9\frac{1}{2}$ turns 28 gauge S.S.C. copper wire, $1\frac{1}{2}$ inches internal diameter. Its inductance is 2.30 microhenries. The reaction coil, R , consists of a similar winding of $7\frac{1}{2}$ turns, approximately 1.5 microhenries in inductance. The auxiliary plate forming the condenser, C , with the test-piece is held in an ebonite frame (fig. 5) which clamps lightly on to the test-piece by ebonite screws. The mica used is .0002 to .0005 in. thick, and the plate .4 in. square.

The valve, V , is a Mullard "Ora," which is found to oscillate easily under adverse conditions. The battery, A , is a four-volt accumulator of 100 ampere hours capacity. This large capacity ensures constancy of filament current, which is a necessity, as the frequency of oscillation is not

quite independent of filament temperature. A switch, S, controls this battery.

A plate voltage of 90 is necessary to enable the valve to oscillate under the adverse conditions obtaining. This is supplied by the dry cell battery, B. A bye-pass condenser, P, of .002 microfarad is connected as shown to enable the high frequency currents to avoid the inductance of the battery B and its leads, and, when used, telephones at T. These terminals are used to insert a pair of telephones for testing purposes only. They are normally short-circuited. The filament battery is connected to the frame of the testing machine as shown at E. The test-piece is, of course, similarly connected by the gluts (fig. 5). Thus the oscillatory circuit L, C, has its lower junction completed through the

Fig. 5.



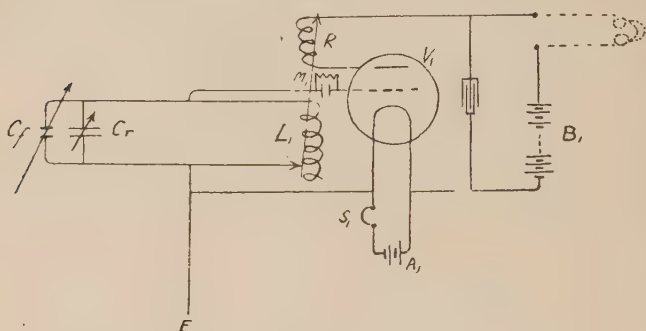
Frame holding auxiliary plate.

condenser P, whose impedance at 10 million frequency is very small. This is preferable to earthing the lower end of L to the testing machine, as the accumulator A would then be at 90 volts negative potential to earth with consequent current leakage from the battery B and possible damage to the cases of the accumulator A. A resistance, M, of several megohms is connected in the grid circuit so as to cause the electronic discharge on to the grid to maintain its mean potential at -6 volts. This compensates for the fact that 90 volts is used on the plate whereas the valve is designed for 30 volts. To prevent high frequency losses in M it is shunted by a condenser of .0005 microfarad capacity. The small size of the reaction coil is necessitated by the fact that the frequency at which the circuit L, C will oscillate is not independent of the natural frequency of the reaction coil given by its inductance, its self-capacity, and the plate-filament capacity of the valve, which acts across it, but is nearly so if this natural frequency is much greater than that of the circuit L, C. The coil used as reaction coil has a natural frequency

of about 50 million when connected to the valve. The coupling between the main inductance and reaction coil is made variable so as to control the amplitude and stability of the oscillations.

The Receiver circuit is shown in fig. 6.

Fig. 6.



Circuit diagram of "Receiver."

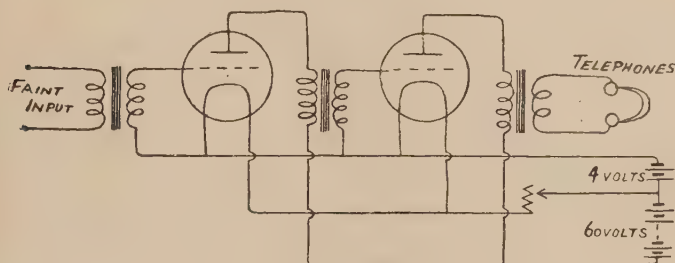
The inductance L_1 consists of a spiral winding of $11\frac{1}{2}$ turns, tapped at $7\frac{1}{2}$, $9\frac{1}{2}$, and $11\frac{1}{2}$ turns so as to give a wide range of frequency and a choice of L/C ratios, which latter is desirable to secure a suitable degree of stability of the oscillations produced. The approximate inductances are 1.4, 2.3, and 3.4 microhenries. The reaction coil R_1 is a spiral winding of 11 turns and inductance approximately 3.3 microhenries. The condenser forming the remainder of the oscillatory circuit is divided into two, C_r , of approximate range .00001 to .0002 mfd., and C_f , approximately .00001 to .00002 mfd. By a system of gearing, this last condenser is made capable of very critical control, and is used for fine adjustment of the frequency.

A French "R" type valve, V_1 , is used in this circuit owing to its all round efficiency. A four-volt accumulator of 100 ampere hours capacity, A_1 , and 60 volt dry battery, B_1 , supply filament current and plate voltage respectively. Rectification of the beats of amplitude of oscillation is provided for by the leak and resistance, M_1 , of $1\frac{1}{2}$ megohms and .0001 mfd. capacity. The unilateral conductivity of the grid-filament space causes alternating voltages applied to the grid from the main oscillatory circuit to give negative charges to the grid varying with their amplitude. This causes non-symmetrical reproduction in the plate circuit which can be resolved into symmetrical and unidirectional components. The unidirectional component affects the

telephones. The mean potential of the grid is maintained at a suitable value by the $1\frac{1}{2}$ megohm leak. The coupling between the main inductance, L_1 , and reaction coil, R_1 , is again made variable so as to afford control of the stability of oscillation.

When the receiver and transmitter are coupled together and adjusted so that their difference of frequency is very small they tend to pull one another into step, and the beat-note disappears. This tendency is reduced by making the coupling between the two units very small, and arranging the stability of oscillation of the two circuits to be approximately the same. It proves necessary to have the receiver and transmitter six feet apart, and to take great care that the loop formed by the earthing and condenser leads on the transmitter is at right angles to the direction of the receiver. This results in a beat-note so faint as to be inaudible above ordinary laboratory noises, and two further valves are therefore used as low frequency amplifiers to give a note of convenient loudness. The diagram of this part of the apparatus is shown in fig. 7.

Fig. 7.

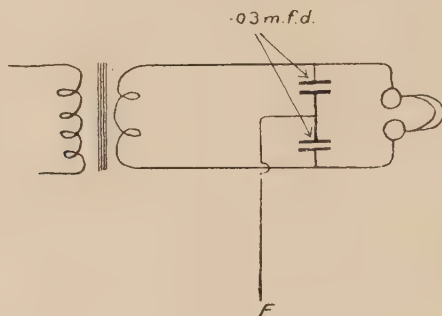


Low frequency amplifier.

Owing to the sensitivity of the apparatus to capacity changes, it is strongly affected by the movement of persons in its neighbourhood. The operator stands on the opposite side of the pillar of the testing machine to that on which the transmitter is placed, the pillar acting as a screen. The operator's body is earthed by the insertion, in the stocking, of copper gauze connected to earth. Since, however, the inductance from hand to foot is not negligible at 10,000,000 frequency, this does not entirely stop changes of beat-note from occurring when the machine is handled. A thick leather glove is therefore worn during tests. It is found necessary to join all metallic masses in the laboratory together and connect them to the filament circuit of the

receiver and to the testing machine in order to avoid changes of beat-note when the operator moves in their neighbourhood. Though removed from the oscillatory circuit by three transformers and two valves, the telephones have sufficient capacity coupling to it to cause changes of beat-note when their pressure on the operator's head varies. They are therefore earthed in the manner shown in fig. 8.

Fig. 8.

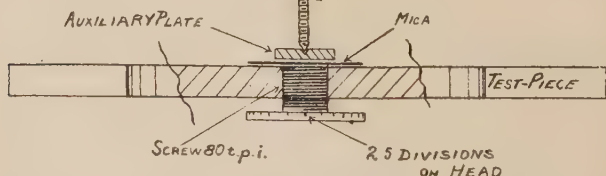


System of earthing telephones.

Photographs of the apparatus are appended (Pl. VI.).

4. The frequency of oscillation is checked before each test by means of a low-range heterodyne wavemeter designed for wireless telegraphy. Readings are taken of the settings of this instrument at which its harmonics are heard in the receiver. These values divided by consecutive numbers, found by trial, give a constant—the wave-length of the set, from which its frequency can be calculated. The wave-length can easily be kept between 35 and 28 metres, corresponding to frequencies of 9.8×10^6 and 12.5×10^6 .

Fig. 9.



5. An approximate estimate of the sensitivity of the instrument has been made in the manner shown in fig. 9.

Artificial distortion of a dummy test-piece is produced by means of a screw of 80 threads per inch let into it. The

The change of capacity of the condenser for a given minute movement of the plates will, as is indeed apparent from the plotted results, be very much greater when they are almost touching the mica than when they are spaced apart from it by only a very small distance. As $1/4000$ and $1/2000$ inch are very large compared with the slip during a test, it is necessary to make use of extrapolation. The curves will be approximately of the same shape as those showing the variation of capacity of a condenser with the distance between its plates, and, using this as a guide, the curves are produced (as shown dotted) till near the line indicating the flush position of the screw face. The maximum rate of change of capacity attainable with the instrument occurs when the metal surfaces are touching the mica. The movement of the screw face has been in air. Hence, on the horizontal scale, the $3/10,000$ of mica used will be represented by $1/20,000$ inch of air, since the specific inductive capacity of mica is about six. Hence, lines drawn parallel to the "flush" line and separated from it by $1/20,000$ inch will cut the extrapolated curves at the value of N/n which would be attained if it were possible to move the screw face through $1/2000$ inch while keeping its average distance from the mica zero.

This intersection occurs at $N/n=2000$.

Thus the sensitivity is

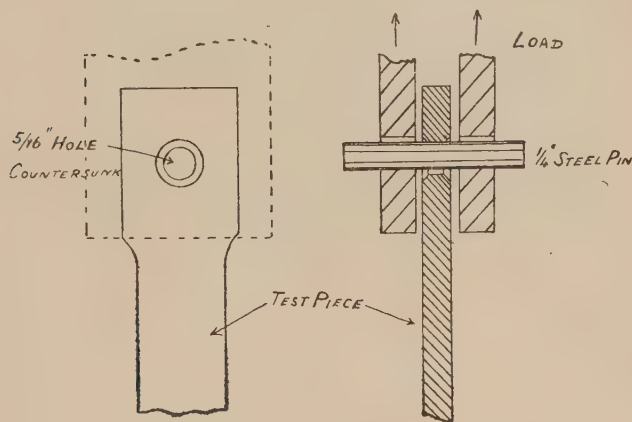
$$\begin{aligned} \frac{n}{N} &\times \frac{1}{2000} \text{ in.} \\ &= \frac{1}{2000} \times \frac{1}{2000} \text{ in.} \\ &= .25 \times 10^{-6} \text{ in.} \\ &= 6.5 \times 10^{-6} \text{ mm.} \\ &= 65 \text{ \AA units.} \end{aligned}$$

Owing to the extrapolation and approximations involved, this figure can only be regarded as a rough indication of the order of magnitude of the smallest slips observed.

6. Two general observations of interest were made with the instrument. Knife-edge friction in the beam-testing machine employed tended to swing the top glut outwards when the beam fell, and inwards when it rose. This caused a slight general bending of the test-piece, which gave a rise of note in the telephones. This rise in note was considerably diminished by dispensing with gluts and loading the test-piece axially in the manner shown in fig. 11.

In an attempt to eliminate it entirely, the auxiliary metal surface used to oppose the test-piece surface was made of tinfoil backed by a block of soft rubber forcibly pressed by a screw on to the face of the test-piece. A rise in note on putting on load was still observed however, and the rise in note was now the same whether the test-piece were loaded axially or not, and even when wedge-shaped packing was put in the gluts to give big bending stresses.

Fig. 11.



Method of applying axial loads.

Provided that the load was not such as to cause the metal to behave non-elastically, the note returned to datum when the load was taken off. It seemed clear that the rubber-backed condenser plate had compensated for general bending of the test-piece, and that the effect was due to elastic inequalities of the surface of the test-piece, caused by the stress applied.

In carrying out ordinary tests, when a load was reached which gave a yield, it was observed that the note in the telephones did not assume its highest pitch at once, but during a period of from half a second to five seconds. The rate of rise was great at first and gradually decreased till imperceptible. That this lag was not due to the testing machine or valve instrument was proved by the rapidity with which elastic strains were indicated. It therefore became apparent that this was an early stage of the time lag which

takes place in a yield, the later stages of which have been described previously ("Surface Tension Effects in the Intercrystalline Cement in Metals and the Elastic Limit," F. C. Thompson, Jour. I. S. I., 1916, No. 1, pp. 186-7).

7. Time was not available for many tests, and in view of the fact that further work is required before they can be discussed from a metallurgical point of view, only a few experimental results are given showing some of the possibilities of the instrument. A 70/30 Brass, in the annealed condition, of maximum stress 10 tons per sq. in. and safe fatigue range (Haigh machine) 10 tons per sq. in., had an elastic limit as determined visually of 2.7 tons per sq. in. The valve slip indicator showed slip at 2.4 tons per sq. in. Annealed 80/20 Cupro-nickel gave very similar results.

A 0.25 per cent. Carbon Open-hearth Steel, normalized, had a maximum stress of 35 tons per sq. in., a safe fatigue range (Haigh machine) of 24 tons, and elastic limit (Metzger Extensometer) of 16 tons per sq. in. The valve slip indicator showed a slip at 14.2 tons per sq. in.

In all the above cases, the valve slip indications were very sharp in character and great in magnitude, and increased rapidly on further loading, up to fracture.

Annealed Copper used had a maximum stress of 15 tons per sq. in., a safe fatigue range (Haigh machine) of 11½ tons per sq. in., and an elastic limit (visually determined), of about 4 tons. With the valve slip indicator it showed faint slip at very low loads of .1 to .4 ton per sq. in. Faint slip continued until a load between 3 and 4 tons per sq. in. was reached, when comparatively sharp and heavy slip, increasing on further loading up to fracture, was observed. Between the point at .1 to .4 ton and that at 3 to 4 tons, the faint slip appeared to be discontinuous, increasing abruptly at two points near 1.2 tons and 2.0 tons per sq. in., but these points were not very sharply marked and their existence is not considered as definitely proved.

Annealed Nickel gave similar results. Very faint slip began at .6 ton per sq. in., and a definite yield occurred at about 6 tons per sq. in. There appeared to be a discontinuity in the slip prior to 6 tons per sq. in., at about 3 tons per sq. in. The maximum stress of this material was 31.2 tons per sq. in., its safe fatigue range (Haigh machine) 37 tons, and elastic limit (visually determined) 25 tons per sq. in.

FIG. 1.

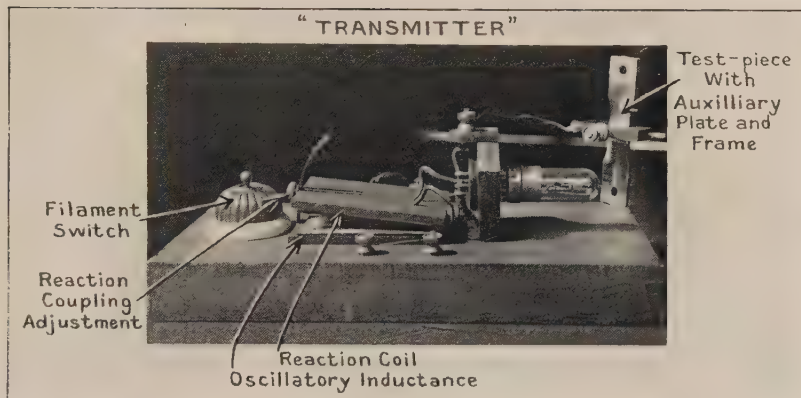
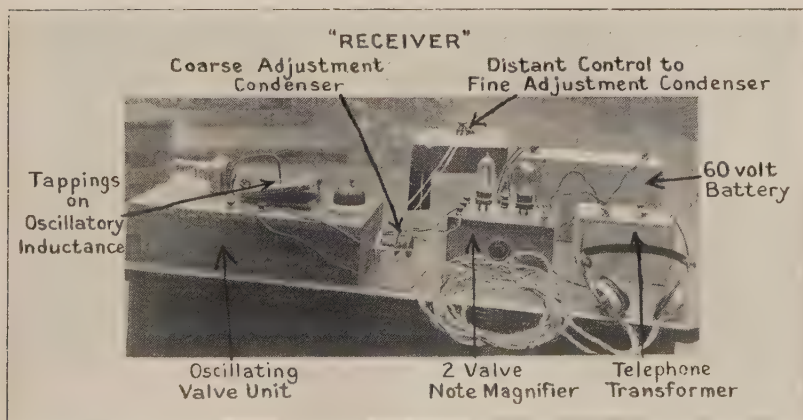


FIG. 2.



8. The work described was done in the Faculty of Metallurgy, University of Sheffield, in 1922, with the aid of a grant from the Department of Scientific and Industrial Research, and under the supervision of Professor Desch.

The author feels very deeply indebted to Professor Desch, whose keen interest and generous aid has contributed very largely to whatever success has been attained.

He desires also to thank the Staffs of the Faculties of Engineering and Metallurgy, who have assisted in many ways, especially by the loan of apparatus, and in the preparation of test-pieces.

LXXXIX. *Determination of the Curvature Invariant of Space-Time.* By L. SILBERSTEIN, Ph.D.*

THE empty space-time which was originally proposed by de Sitter as a solution of Einstein's amplified field-equations, and which possesses the more important property of being perfectly isotropic with respect to Riemannian curvature, is characterized by the line-element

$$ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - dr^2 - R^2 \sin^2 \sigma (d\phi^2 + \sin^2 \phi d\theta^2), \quad (1)$$

where $\sigma = r/R$. The space-part of this quadratic form is the line-element of an elliptic space which will be assumed to be of the *polar* or properly elliptic kind, so as to be covered by the interval $\sigma = 0$ to $\sigma = \frac{1}{2}\pi$. The constant R is the curvature radius of this space (as a particular section of the fourfold) and, what is more important, an *invariant of the space-time*; if G be the invariant of the curvature tensor G_{ik} , the radius R as appearing in (1) is given by $G = 12/R^2$. In fine, R has an intrinsic meaning and, if it is at all finite, it is manifestly of prime interest to determine it from a number of independent sets of observational data and to see whether the R -values thus obtained are more or less consistent with each other.

It is the purpose of this paper to show that such is very likely the case. Very likely, that is, inasmuch as the now available data yield, with the aid of a Doppler effect formula to be derived presently, nine R -values, seven from globular clusters and two from the Magellanic Clouds, which seem to be fairly consistent with each other and do not clash with the generally accepted views of the known universe.

* Communicated by the Author.

De Sitter's own attempt to that effect is well known from his paper (M. N., R.A.S., Nov. 1917) and from text-books on Relativity. It was based on the artificial assumption of a star coerced to remain at a fixed distance r from the observer, and led to a spectrum-shift or, as we will henceforth say, a *Doppler effect* *, $D = \delta\lambda/\lambda$, which by the first term of (1) should be

$$D = \frac{1}{\cos \sigma} - 1 \doteq \frac{1}{2} \sigma^2.$$

The characteristic feature of this formula was that it predicted always a positive D or a *red-shift*. Its application to the B -stars, which show such systematic shifts of about 4.5 km./sec., gave $R = 6.7 \cdot 10^9$ astr. units, one third of the effect being attributed by de Sitter to the gravitation fields of the stars themselves. Apart from being too small, this value stood alone, not being supported by other values derivable by means of the same formula from other celestial objects. The Lesser Cloud, as quoted by de Sitter *loc. cit.*, rather contradicted the B -stars' value, offering one of the order 10^{11} at the least. The important point, however, is that de Sitter's formula cannot be applied to actual stars, if these, as well as the observing station, are to behave as free particles, describing world-geodesics. For such particles cannot, in the space-time (1), be at rest relatively to each other even a single instant, unless they coalesce or one is at the polar of the other. Thus, to be of any use at all, the Doppler effect formula ought to be constructed for a star and an observer in free inertial motion, each describing some geodesic $\delta \int ds = 0$ of de Sitter's space-time (1) or, in view of the practically evanescent transversal effect, a geodesic of its two-dimensional section

$$ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - R^2 d\sigma^2, \quad . \quad . \quad . \quad (1a)$$

covering the sub-case of all radial motions.

This broader problem was recently taken up by Weyl †, whose merit it is to have formulated a general principle for computing intrinsically any such Doppler effect. The principle, which naturally suggested itself, is

$$D = \frac{ds}{ds'} - 1, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* Whether it be associated with a relative motion of source and observer or not.

† *Raum-Zeit-Materie*, 5th ed., 1923, Anhang iii., and *Phys. Zeitschr.* 1923, p. 230.

where ds is the element of the observer's world-line cut out by the light-cones (in the present case the minimal lines of the twofold r, t) having their apices at the points s' and $s' + ds'$ of the star's world-line. The meaning of the formula is obvious, ds/ds' being the ratio of the proper times of the receiver and the sender. Its validity for actual spectrum comparisons is, of course, conditioned by the hypothetical permanence of atoms as "natural clocks" in Einstein's sense of the word, a much debated hypothesis which will here be accepted.

Unfortunately, applying this general principle (2) to the problem in hand, Dr. Weyl introduced the perfectly gratuitous assumption, more or less disguised as a necessary feature of de Sitter's world, according to which the world-lines of all the stars belong to a "pencil of geodesics diverging towards the future"—which, in plain English, amounts to assuming that some time ago the stars were all assembled and rather crowded around some place and had, there and then, evanescent relative velocities, to grow later on into huge and (apart from gravitation) ever increasing positive radial motions. With this arbitrary hypothesis, and through a number of rather obscure technicalities*, Weyl's formula became

$$D = \tan \sigma,$$

with a unique positive sign, yielding always a red-shift or what the astronomers call a *positive* "radial velocity." Dr. Weyl himself insists on this feature as a result of his sublime guess about the remote past of all the stars. An echo of this "universal scattering tendency" of matter resounded in Eddington's 'Mathematical Theory of Relativity,' where some curiously fallacious remarks are made in connexion with this subject. But, no matter how unlikely and how arbitrary, Weyl's hypothesis is entirely undesirable, as it is flatly contradicted by the famous nebula in Andromeda, showing an effect of $cD = -300$ or -316 km./sec., by one or two more spirals, though these do show a preponderance of positive or red-shifts, and by a host of equally interesting and probably as distant celestial objects, the globular clusters. Among the latter, negative radial velocities are by no means an exception. Rather the contrary.

Under these circumstances it has seemed worth while to

* Some of these, which the reader may try to extricate, *loc. cit.*, are responsible for 'tan' instead of $\sin \sigma$; but this is of little importance, as in all hitherto accessible cases both reduce to σ .

investigate the problem from the outset, basing its solution on de Sitter's theory unsupplemented by any such arbitrary assumptions by which it was unnecessarily limited or actually mutilated.

The equation of a geodesic of the twofold (1 *a*), representing the most general radial motion of a free particle, is easily found to be

$$\frac{R}{c} \frac{d\sigma}{dt} = \pm \cos \sigma \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2}} \equiv \pm \frac{\eta}{c}, \quad . \quad . \quad . \quad (3)$$

where the signs correspond to a receding and an approaching particle respectively, and γ is an integration constant, $\cos \sigma \cdot c dt/ds = \gamma$, which, with β written for v_0/c , has the meaning

$$\gamma = (1 - \beta^2)^{-1/2},$$

and is, therefore, essentially greater than, though but slightly differing from, unity. Thus, as mentioned before, v can be zero only for $\sigma = 0$ or $\sigma = \frac{1}{2}\pi$. At any intermediate distance the two particles, say at $r = R\sigma$ and at $r = 0^*$, have necessarily some non-vanishing, either receding or approaching, radial motion relatively to each other. The corresponding acceleration is, still rigorously, determined by

$$\frac{R^2}{c^2} \frac{d^2\sigma}{dt^2} = \frac{1}{2} \sin 2\sigma \left(\frac{2 \cos^2 \sigma}{\gamma^2} - 1 \right), \quad . \quad . \quad . \quad (4)$$

with the same sign for both receding and approaching motion. Thus, up to a distance $\sigma_1 = \arccos(\gamma/\sqrt{2})$, which practically will be but little below 45° , the two particles do in fact behave as if they repelled each other. This, however, does not prevent the motion being, at any distance, either an approaching or a receding one. Moreover, beyond σ_1 or, practically, beyond the midpoint between the observer and his polar the acceleration itself of, say, a star will be negative, as if it were attracted by the observer †. At any rate, there is not the slightest reason for excluding negative velocities. It is true that a star which left the observer with an almost evanescent radial velocity ($v_0 \doteq 0$, $\gamma \doteq 1$) would continue to recede from him with a velocity growing up to $r = \frac{c}{2}$

at the midpoint, then only to fall off towards the polar. But, in quite the same way, one that left the polar with an almost evanescent velocity would approach us with a velocity

* Notice that $r = \text{const.} = 0$ is one of the world-geodesics (3).

† Notice in passing that the volume of the sphere $\sigma = \frac{\pi}{4}$ bears to that of the remaining elliptic space the ratio $(\pi - 2) : (\pi + 2)$. Thus, if the stars are more or less uniformly distributed, there are to every 'repelled' star about five which behave as if 'attracted' by the observer.

increasing up to the midpoint and then decreasing, yet still retaining an enormous negative value until it almost reaches us. In fine, any particular case of receding motion is perfectly reversible and may, as such, be represented among the stars. But enough has now been said against that mythical "divergence towards the future."

To proceed with our subject, notice for the sequel that eq. (3) assumes for $\gamma=1$ ($v=0$) the simple form

$$\frac{R}{c} \frac{d(2\sigma)}{dt} = \pm \sin 2\sigma, \dots \dots \dots (3_0)$$

and similarly (4),

$$\frac{R^2}{c^2} \frac{d^2(4\sigma)}{dt^2} = \sin 4\sigma. \dots \dots \dots (4_0)$$

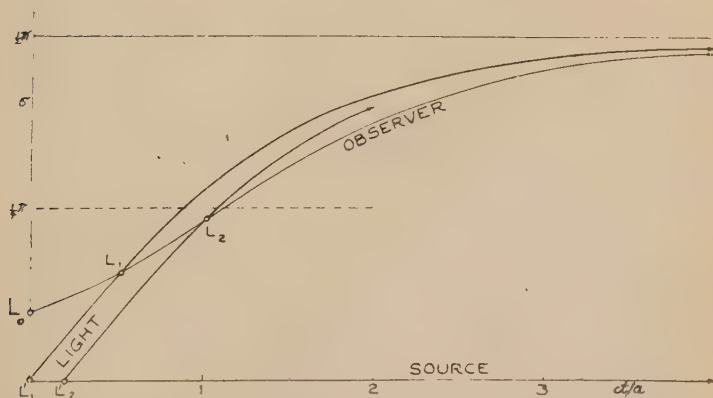
The equation (3₀) as well as (3) can at once be integrated in terms of trigonometric functions, but their integral forms will not even be needed for the problem in hand. In fact, reserving $r=0$ for the world-line L' of the star, let the observer's world-line L be any of the geodesics (3), *i. e.*,

$$\frac{ct}{R} = \int_{\sigma_0}^{\sigma} \frac{\sec \sigma d\sigma}{\sqrt{1 - \cos^2 \sigma / \gamma^2}}. \dots \dots \dots (L)$$

The line representing the star's light signal emitted from L_1' , say at the instant $t=\alpha$, is

$$\frac{c}{R}(t-\alpha) = \int_0^{\sigma} \sec \sigma d\sigma.$$

Fig. 1.



The world-point L_1 being the intersection of L with this line, its coordinates r, t are determined by the last two equations. The relations are represented on the figure, which is drawn correctly for the sub-case $\gamma=1$, and for

a receding motion *. Imagine the last two equations solved for t , σ and differentiated with respect to α , another signal being sent, from L_2' , at $t = \alpha + d\alpha$. Then

$$c(dt - d\alpha) = \sec \sigma \cdot dr, \quad cdt = \frac{\sec \sigma \cdot dr}{\sqrt{1 - \cos^2 \sigma / \gamma^2}},$$

two equations for cdt and dr , the components of the element $L_1 L_2$ or ds in terms of $cd\alpha = ds'$, the line-element of the source. Solving these and substituting in $ds^2 = \cos^2 \sigma \cdot c^2 dt^2 - dr^2$, we have the required ratio of proper times,

$$\frac{ds}{ds'} = \frac{\cos^2 \sigma / \gamma}{1 \pm \sqrt{1 - \cos^2 \sigma / \gamma^2}} = \gamma [1 \pm \sqrt{\text{idem}}].$$

Whence, by (2), the required formula for the complete Doppler effect,

$$D = \gamma \left[1 \pm \sqrt{1 - \frac{\cos^2 \sigma}{\gamma^2}} \right] - 1, \quad . \quad . \quad . \quad (5)$$

where $r = R\sigma$ is the observer's distance from the star at the moment of receiving its light. For, referring to the figure, σ was the ordinate of L_1 . The distance σ_0 at the moment of emission would be given by $L_1' L_0$ and is readily expressed in terms of σ . But the latter enters in a much simpler way into the expression of the Doppler effect, and will therefore be retained throughout the investigation. The upper sign in (5) holds for a receding, and the lower for an approaching star. We may write equivalently, by (3),

$$D = \gamma \left[1 \pm \frac{v}{c} \sec \sigma \right] - 1,$$

* This figure is also instructive in another way. It shows that the geodesics $\gamma = 1$, such as the "observer's" line $L_1 L_2$, have an inflexion-point at $\sigma = \frac{1}{4}\pi$. There the relative velocity reaches the maximum $c/2$, and the acceleration is changed from repulsive to attractive. Again, it exhibits the light-lines $L_1' L_1$, $L_2' L_1$ as asymptotic to the polar $\sigma = \frac{1}{2}\pi$. If, therefore, the observer happens to be at the polar of the star, and *vice versa*, the ratio ds/ds' of the corresponding segments ($L_1 L_2$ and $L_1' L_2'$) need not vanish, but is, to begin with, indeterminate. It acquires a definite value only when considered as the limit for a geodesic, such as $L_1 L_2$, tending to the polar, and then the limiting value of the ratio is either 2 or zero, according as we approach the line $\sigma = \frac{1}{2}\pi$ through geodesics representing a receding or an approaching motion, respectively. This disposes of the prejudice, repeated after de Sitter by all authors, as to the "complete standstill" at the observer's polar, derived hastily from (1) by putting $\sigma = \frac{1}{2}\pi$. The "standstill" exists only analytically when judged by the coordinate-time t . It disappears when we estimate the succession of events at the polar by the ratio based on light-signals, the only means of knowing anything about these events.

which, apart from $\sec \sigma$, will strike the reader as a more familiar form.

Formula (5) holds rigorously, for any value of the integration constant β entering through γ which, for all we know, may differ from star to star. Thus, the Doppler effect is, in general, by no means a universal function of distance alone. If we were to judge from most of the near stars, β^2 might be an exceedingly small fraction. Yet, no matter how small, it cannot in general be wholly disregarded, unless σ begins to amount to something. So much so, in fact, that for near stars it is β which plays the chief rôle, while $\cos \sigma$ can be confounded with unity, thus leading from (5) to

$$D = \sqrt{\frac{1 \pm \beta}{1 \mp \beta}} - 1,$$

the well-known formula of the special relativity theory. If here β^2 and higher terms be neglected, we are at once reduced to $D = \pm v_0/c$, which is the classical formula. It will be noticed that the equation of inertial motion, (3), gives for small σ a type of motion which is within short intervals of ct/R approximately uniform, with v_0 as velocity. In fine, as far as small-scale phenomena are concerned, Newton's law of inertia and the ordinary Doppler formula come to their rights. For somewhat more distant celestial objects both σ and β may have to be retained, under the radical, that is. In γ as factor of the bracketed expression in (5) the term β^2 can at any rate be neglected so that we are left with

$$D = \pm \sqrt{1 - \cos^2 \sigma / \gamma^2} = \pm \sqrt{\sin^2 \sigma + \beta^2 \cos^2 \sigma}, \quad (5a)$$

or, for σ not exceeding a few degrees (which, however, will be seen to cover even all the extra-galactic objects hitherto explored), with more than sufficient accuracy,

$$D = \pm \sqrt{\sin^2 \sigma + \beta^2}. \quad (5b)$$

Here, for the great majority of intergalactic stars, both terms have to be retained (of course, with $\sin \sigma \doteq \sigma$), and the writer hopes to give some applications of this formula, in connexion with statistical considerations relating to comparatively near stars, at a future opportunity.

Meanwhile, aiming at the most remote objects of the sky, we tentatively consider β^2 as altogether negligible in presence of unity, and even of $\sin^2 \sigma$, so that $\gamma \doteq 1$. Then

formula (5) will assume the simple form

$$D = \pm \sin \sigma = \pm \frac{r}{c} \sec \sigma, \quad . \quad . \quad . \quad (5c)$$

the latter by (3). Notice in passing that, if a be the usual astronomical unit of length, de Sitter's parallax formula is

$$p \doteq \tan p = \frac{a}{R \sin \sigma}. \quad . \quad . \quad . \quad (6)$$

so that the last formula can also be written, removing every doubt as to the physical meaning of ' r ,'

$$Dp = \pm \frac{a}{R}. \quad . \quad . \quad . \quad (5d)$$

Keeping this in mind we may, however, retain the co-ordinate-distance r , especially as the larger distances are certainly not estimated by trigonometric parallaxes. At any rate, since the largest Doppler effect ever observed, namely +1800 km./sec. shown by the spiral nebula N.G.C. 584, still amounts to $D=6 \cdot 10^{-3}$ only, we may as well confound $\sin \sigma$ with σ and write

$$D = \pm \frac{r}{R}, \quad . \quad . \quad . \quad (5e)$$

the coordination of signs being as before.

Now, D -values, all large enough, are reliably measured for some forty spiral nebulae. Unfortunately, however, as I am advised by Prof. Shapley, no good distance estimates of these fascinating objects are as yet available. Even in the case of the great nebula in Andromeda the distances found are so widely discrepant as 200,000 and 2800 parsecs, both estimates derived by Lundmark, quoted occasionally by Russell and by van Maanen, respectively. Jeans puts it even at 1700 parsecs only. Moreover, a single R -value derived from the data for the Andromeda nebula or any such object, even if it seemed of a reasonable order, would not, of course, speak either for or against the formula and the theory from which it was derived. A crucial test will consist in applying (5e) to a number of distant celestial objects for which tolerably reliable pairs of data r, D are available. Since the spirals do not as yet offer such an opportunity, let us turn to the globular clusters. The "radial velocities" of these systems are known only with a P.E. which it is, according to a private letter of Prof. Shapley, a fair guess to put at 25 to 50 km./sec. Yet, since their distances were rather consistently estimated, a test of our formula may be attempted on this class of celestial objects.

Shapley's paper in vol. xlix. of the *Astrophys. Journal*, p. 322, contains a table of ten globular clusters with both r and D values. In view, however, of the large probable errors of D , just mentioned, only those clusters seem worth considering whose measured radial velocities cD are not much below a hundred km. per sec. We are then left, for the present, with only seven clusters.

These give the following table, in which "radial velocities" are in km./sec., the corresponding D 's being simply their values divided by c , and r as well as the quotients $R=r:D$ are in astronomical units :—

Cluster, N.G.C.	r .	Rad. velocity.	$D \cdot 10^5$.	$R \cdot 10^{-12}$.
5024	38.10 ⁸	-170	- 57	6.7
5272	28 „	-125	- 42	6.7
6205	22 „	-300	-100	2.2
6333	50 „	+225	+ 75	6.7
6341	25 „	-160	- 53	4.7
6934	67 „	-350	-117	5.7
7078	29 „	- 95	- 32	9.1

The consistency of the figures of the last column, with a mean of

$$R = 6.0 \cdot 10^{12},$$

is, perhaps apart from the third item, surprisingly close, and in view of the large P.E. of the measured spectroscopic shifts (due to the very low dispersion necessary to photograph these objects at all) even better than one would feel entitled to expect. It goes without saying that many more data would be desirable before forming a final judgment. Yet, this little table, as it stands, seems encouraging, as speaking rather in favour of formula (5e) and thus also for de Sitter's cosmology. It will be well to remember that the early determinations of the electronic e , for instance, differed from each other not less than these seven values of the curvature invariant of space-time. Again, very much as in the case of the electronic and other "universal constants," the knowledge of R in itself is not so important as the law which is implied by the consistency of the several R -values. This law, subject, of course, to many further tests, may be concisely formulated, in terms of physical magnitudes alone, as follows :—

The product of the numerical value of the Doppler effect into the parallax of a distant star is a constant, viz. the smallest parallax possible.

For, according to the parallax formula (6), a/R is precisely

this minimum parallax ρ_m , attained at the polar, so that the law, yet to be tested, can be written

$$D\rho = \pm \rho_m \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

With the above value of R we should have $\rho_m = \frac{1}{6} 10^{-12}$ radians or $3''.44 \cdot 10^{-8}$.

To the meagre table upon which this provisional value is based but two more items can for the present be added. The Lesser Magellanic Cloud shows an effect of $+150$ km./sec. According to Hertzsprung its distance exceeds 10,000 parsecs, while Shapley's more recent estimate is 20,500 parsecs, which may here be adopted. The radial velocity of the Greater Magellanic Cloud is, according to Wilson, $+276$ km./sec., and its distance, according to Shapley, 61,000 light-years*. Thus, by (5e), we have

$$\text{from the Lesser Cloud} \quad . \quad . \quad . \quad R = 8.2 \cdot 10^{12},$$

$$\text{and from the Greater Cloud} \quad . \quad . \quad R = 4.2 \cdot 10^{12},$$

not clashing with the values derived from the globular clusters. The mean of all the nine values is

$$R = 6.05 \cdot 10^{12},$$

not differing materially from the previous one.

It is hoped that a further extension of the list, which may either discredit or strengthen the proposed formula, will soon become possible.

Returning for a moment to the spiral nebulae, for which no independent distance estimates will soon be available, we may provisionally adopt the value $R = 6 \cdot 10^{12}$ in order to obtain a preliminary idea of their distance, putting, that is, in astronomical units,

$$r = 6 \cdot 10^{12} | D |.$$

Thus, for instance, the Andromeda nebula, for which Slipher finds -300 and Pease -316 km./sec., would have to be placed at a distance of 6.0 to $6.3 \cdot 10^9$ astr. units, or, in round figures, 30,000 parsecs, which seems to fall between the extreme rough estimates occasionally quoted. The most distant spiral thus far explored would be N.G.C. 584 which shows a "radial velocity" of $+1800$ km./sec. or $D = 6 \cdot 10^{-3}$, the greatest effect ever recorded. This nebula would be placed at a distance

$$r = 3.6 \cdot 10^{10}$$

or 180,000 parsecs. Huge as this may seem, it will be

* R. E. Wilson, 'Publications of the Lick Observatory,' vol. xiii. part v. p. 187 (1918). Harlow Shapley, *Astroph. Journ.* xlix. p. 322 (1919).

remembered that Shapley's latest estimate of the semi-diameter of our galaxy is only four times smaller. Next would come the spiral N.G.C. 936, with the (doubtful) effect $+1300$ km./sec., at a distance $r=2.6 \cdot 10^{10}$. Similarly for the remaining spirals tabulated by Slipher and given in Eddington's book. Whether these estimates will or will not fit into the general scheme of modern galactic and extra-galactic astronomy, is not known to me and must be left to the scrutiny of the specialists.

The very probable existence of a large number of galaxies similar to (though, according to van Maanen, not many as large as) our own galaxy would not clash with such a world radius as $6 \cdot 10^{12}$. In fact the total volume of the elliptic space, which is but a particularly simple section of de Sitter's fourfold, being $V=\pi^2 R^3$, and our own galaxy being roughly representable as an ellipsoid of semiaxes $A=B=10$ (' $=9.5 \cdot 10^9$ astr. units, its volume would bear to V , very nearly, the ratio

$$V_g/V = \frac{2}{15\pi} \left(\frac{A}{R}\right)^2,$$

which, with $R=6 \cdot 10^{12}$, is as small as $\frac{1}{6} 10^{-9}$. There would thus be room enough for hundreds of millions of such systems with ample intergalactic spaces. Moreover, when judged by the time succession of light-messages from further and further objects, up to our polar, our universe would to all purposes be rigorously infinite, thus not thwarting even the most sublime of our cosmic emotions, to use a word and a concept dear to W. K. Clifford.

My thanks are due to Prof. Harlow Shapley, of the Harvard College Observatory, for aiding me most kindly in extending that minute table.

Rochester, N.Y.,
January 23, 1924.

Note added in Proof reading, March 15, 1924.

The list of nine given above can just be supplemented by one more R -value. For the globular cluster Messier 12, or N.G.C. 6218, Sanford (Mt. Wilson Annual Report for 1919, p. 250) has found $cD=+160$ km./sec., and its distance is estimated by Shapley at 12,400 parsecs, whence, by (5 e),

$$R=4.8 \cdot 10^{12} \text{ astr. units.}$$

It will be noticed that this cluster, being placed at much the

same distance as our previous N.G.C. 6341 (12,300 parsecs) shows a Doppler effect of the opposite sign, but of just the same absolute value, in agreement with (5e).

The ten R -values thus far obtained from the clusters N.G.C. 5024, 5272, 6205, 6333, 6341, 6934, 7078, 6218 and the Lesser and the Greater Magellanic Clouds are, respectively,

6.7 6.7 2.2 6.7 4.7 5.7 9.1 4.8 ; 8.2 4.2 . 10^{12} astr. units.

If, as was tentatively assumed, β^2 is for all these objects actually negligible in presence of σ^2 , the differences between these ten R -values can be attributed to the observation errors of the data, and we may strike an average of the ten determinations; which would give $R=5.9 \cdot 10^{12}$ or, in round figures, *six million million* astr. units.

If, on the other hand, we return to the more accurate formula (5b), and if each of the ten pairs of observations is considered to be materially correct, we are, in our present ignorance of the individual β 's, entitled only to conclude that

$$R = r / \sqrt{D^2 - \beta^2} \geq r : D,$$

that is, $R \geq 9.1 \cdot 10^{12}$, with a strong likelihood, however, that R is not much greater than 10^{13} . (Cf. in this connexion a letter to the Editor of 'Nature,' dated March 3.)

A possible method of clinching the question, *i. e.* of determining β and σ separately, and thus also of deriving the radius R from less distant stars, for which D and r can be more accurately measured, will be described in a later communication.

XC. *An All-metal High-vacuum Pump System.* By
IVOR BACKHURST, M.Sc., and G. W. C. KAYE, O.B.E.,
M.A., D.Sc. (From the National Physical Laboratory*.)

I. INTRODUCTORY.

THE two conspicuous advances in the more recent history of high-vacuum production are doubtless (a) the use of liquid air and charcoal, a method due, as is well known, to the late Sir James Dewar; and (b) the invention of the condensation pump by Langmuir.

The charcoal and liquid air method was the standard method of producing high vacua, from its discovery in 1904 until the development of the condensation pump in 1916.

* Communicated by the Director.

The charcoal method is capable of affording extreme vacua, but at the lower pressures the method is normally slower than the condensation pump.

The different types of high-vacuum pumps available at the present time may be conveniently divided into four classes:—(1) Oil-sealed pumps; (2) Mercury-sealed pumps; (3) High-speed mechanical pumps; (4) Mercury-vapour pumps.

(1) *Oil-sealed Pumps.*

These are mechanical and fall into two divisions:—

(a) *Piston.*—The earlier vacuum pumps were all of the piston type and in the Geryk¹ pattern are still much used.

(b) *Rotary.*—The rotary oil pumps first designed by Gaede², although probably foremost for medium vacuum work, are not generally adopted for pressures above 1 mm. or so, but rather are used to obtain pressures of the order of 0.001 mm. when supported by a piston-pump capable of reducing the pressure directly from atmospheric to about 0.1 to 2 mm. The rotary pumps are, however, slow in dealing with vapours and the oil is apt to become contaminated. The vibration they occasion is considerable, and it is important to protect them against water vapour by the use of drying-tubes. The provision of a by-pass tap and a trap is advisable to assist in preventing overflow of oil in the event of the back-pressure rising or a sudden leak developing in the apparatus to be exhausted. The speed, as defined by Gaede (see p. 925), is from 100 to 150 c.c./sec.

(2) *Mercury-sealed Pumps.*

The simplest pump of the mercury-sealed type is the *Sprengel*³ which depends on liquid-jet action and, according to Kahlbaum, is capable of reaching a pressure lower than 10^{-5} mm.

The *Töpler*⁴ pump, a simple piston-pump in which mercury is used as the piston, is capable of doing nearly as well, and was formerly almost exclusively employed in laboratories devoted to electric discharge-tube research. Both this and the Sprengel pump require constant attention and are extremely slow and, on this account, they are now comparatively little used.

The *Gaede*⁵ rotary mercury-pump, consisting essentially of an Archimedean screw having its axis horizontal and immersed in mercury to a level somewhat above the axis,

is faster than either of the above and requires little attention when motor driven. Its speed is about 100 c.c./sec. It requires a fore-vacuum of about 10 mm. and a by-pass for the supporting pump is necessary. Vapours are pumped very slowly and drying-tubes are required. Although the rotary mercury-pump has been used in many modified forms since it was designed in 1905, it has given place in factory work during the last few years to the rotary oil-pump.

(3) *High-speed Molecular Pumps.*

The molecular pump, invented by Gaede⁶, consists of a grooved cylinder, designed to rotate at about 10,000 revs./min. with a clearance of the order of 0.01 cm. inside a cylindrical casing in which are narrow radial extensions protruding into the grooves. On either side of the extensions are inlet and outlet ports connected in series fashion. The pumping action depends on the fact that in confined spaces at low pressures the collisions of a molecule with the boundary walls are much more frequent than with other molecules. It follows that if one of the walls is in motion, the molecules tend to take up rapidly the direction of this motion. At low pressures the pump maintains a definite ratio between the pressures on either side of it, the value of the ratio for a given speed of rotation and the same gas or vapour depending only on the dimensions of the pump. The value of the ratio may be as much as 100,000. The speed of pumping for air may reach 1400 c.c./sec. at about 0.01 mm. pressure, but falls off rapidly at lower pressures.

* A type of molecular pump, incorporating a number of improvements, has been designed by Holweck¹³.

(4) *Mercury-vapour Pumps.*

(a) *Diffusion pump.*

The mercury-vapour diffusion pump, also first designed by Gaede⁷, is a true diffusion pump, mercury-vapour and air diffusing through a narrow slit in *opposite* directions. The vapour, after passing the slit, is condensed and returned to the boiler, while the air passing through to the opposite side of the slit is carried away by the supporting pump. The high vacuum is thus on the condenser side of the slit. A great disadvantage is that for efficient operation the pressure of the vapour at the slit must be only slightly in excess of that

* Added January 1924.

of the fore-vacuum, so that the temperature of the mercury must be carefully regulated. The pump is also slow, the speed not generally reaching 100 c.c./sec. The advantages of the diffusion pump are that there is no theoretical limit to the lowest pressure attainable, and also that vapours are dealt with as well as gases. These advantages are, however, common to all the various forms of mercury-vapour pumps.

(b) *Condensation pumps.*

In the form of "condensation" pump devised by Langmuir⁸, a blast of mercury vapour is directed tangentially against a water-cooled surface, along which the gas to be pumped is driven. The action depends on the energy of the mercury molecules "reflected" from the cooled surface being too small and non-directive to interfere with the direct blast. The pump is extremely fast, its speed being 3000-4000 c.c./sec. Moreover, the temperature-control is not critical. A fore-vacuum of 0.001 to 0.01 mm. is generally used, the upper limit being about 0.1 mm., and, as already mentioned, the theoretical limit of the pressure obtainable is zero.

Several modifications of the Langmuir type of pump, making use of the jet principle (as in a steam ejector), have proved very successful, such as Crawford's⁹ parallel-jet pump, and the two-stage pumps of Stimson¹⁰ and Volmer¹¹, on the rapidity of which we have no quantitative information. In a two-stage pump the pressure of the fore-vacuum need not be less than a few millimetres, so that a simple piston oil-pump is the only auxiliary required. In each of these modifications the conditions require a fine annular clearance round the jet. So far, jet pumps, owing to difficulties in design, have been constructed only of glass or silica and have not, to our knowledge, been made of metal. The fragility of a glass or silica pump system, while not so important in a research laboratory, is, however, an admitted disadvantage from the industrial point of view.

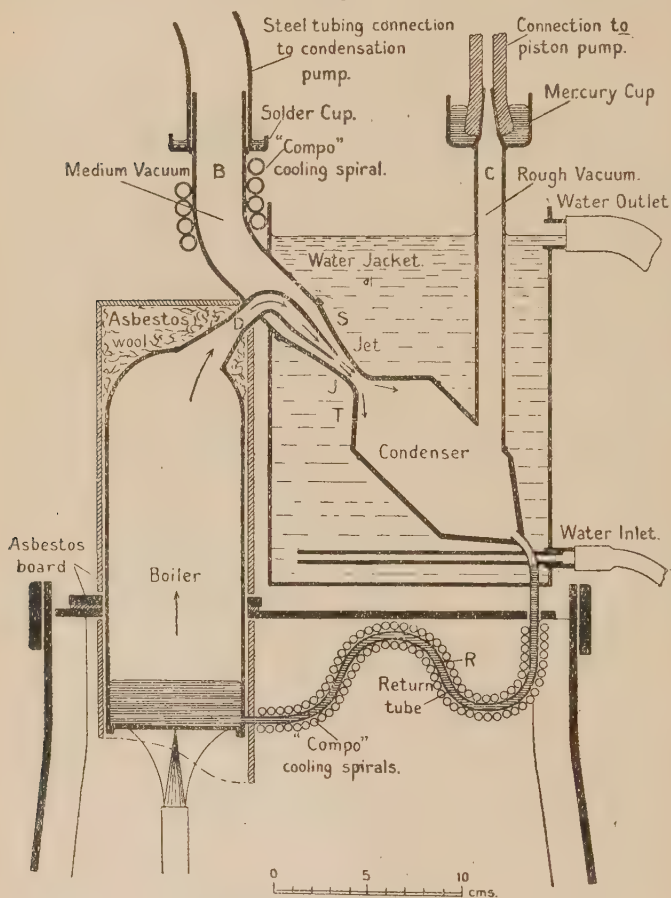
II. DESCRIPTION OF APPARATUS.

The pump system about to be described is of the two-stage type, constructed wholly of metal and consisting of (1) a mercury-vapour jet pump in series with (2) a mercury-vapour condensation pump. It may perhaps be urged that there is no real demarcation between the two types of pumps, but the terms are convenient.

(1) *Mercury-vapour Jet Pump.*

The essential features of the first-stage vapour pump are shown in fig. 1, which is drawn to scale and is almost self-explanatory. The pump is made of steel, mainly from tubing, and all joints are welded*. Our experience is that,

Fig. 1.



Mercury-vapour Jet Pump.

unless welding is carried out by a welder fully accustomed to this class of work, the resulting joints are apt to be porous. We have found that the best remedy for this is thorough nickel-plating.

The boiler is lagged with asbestos board and wool. The

* Brazing is objectionable since it causes gradual contamination of the mercury, while the brazing itself is liable to become porous.

condenser is surrounded by a water-jacket, as shown, and in addition it was found essential to cool the return tube R, which can be conveniently done by the use of coils of "compo" tubing. Two or three turns of cooling spiral are also wound round the tube B on the medium vacuum side. When the pressure in the pump has been reduced to 4 mm. or less, by means of a piston-pump, the jet pump is set in operation by turning on the circulating water and setting a small Bunsen burner under the boiler, the latter containing about $1\frac{1}{2}$ kgms. of mercury. A pointed flame prevents excessive bumping, and in practice a $\frac{3}{8}$ inch diameter Bunsen burner, working under a gas pressure of 4 cm. of water, is found to be convenient. If the pressure at C is about 2 mm., the pressure at B will be reduced to less than 0.001 mm.

The action of the pump is as follows:—Vapour leaves the boiler by the tube D, which is streamlined as far as is practicable, and decreases in cross-section up to the nozzle at J. The mercury vapour issues as a divergent jet, the outer portions of which strike against the water-cooled throat T. Gas or vapour diffusing from the annular space S is caught in the jet and carried into the condenser, and so to the piston pump, while the condensed mercury returns to the boiler through the tube R. The action of the pump is mainly that of the ejector, but utilizes also the condensation principle.

In determining the dimensions of the jet pump, the following points have received attention:—

(1) The boiler is designed to be of sufficient cross-section to allow an adequate rate of evaporation without recourse to excessive temperature and vapour pressure.

(2) The height of the boiler is determined by the necessity of allowing for:—

(a) Vertical height of the condenser.

(b) Difference of level between mercury in return tube near condenser and mercury in the boiler.

(c) Sufficient depth of mercury in the boiler.

(3) The tube leading to the nozzle and the nozzle itself are everywhere streamlined as far as practicable.

(4) The slope of the nozzle, throat, and condenser is everywhere arranged to be sufficient to ensure the flow of condensed mercury to the return tube.

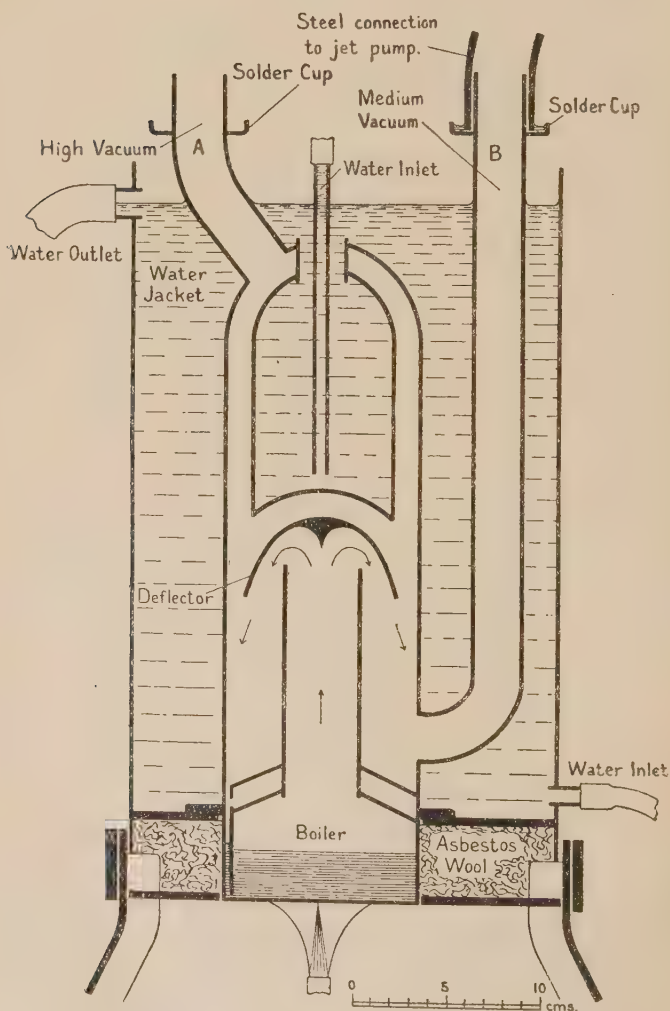
(5) The clearance between the throat and nozzle has to be small, although the cross-sectional area of the nozzle could be increased considerably beyond that shown, providing that the boiler were capable of supplying a sufficient stream of vapour.

(6) The neck has to be prolonged sufficiently beyond the nozzle to avoid the return of air past the jet.

(7) The water-cooling is extended well back behind the mouth of the nozzle to promote efficient operation.

(8) The surface-area and volume of the condenser and the cross-section of the return tube have to be adequate.

Fig. 2.



Mercury-vapour Condensation Pump.

(2) *Mercury-vapour Condensation Pump.*

The second-stage vapour pump is shown to scale in fig. 2, and is substantially as designed by Langmuir. It is made of steel tubing, the joints being welded and the whole nickel-plated. Since the pressure of the vacuum produced by the jet pump is as low as 0.001 mm., it is possible for the clearance between the deflector and the surrounding pump cylinder to be made wide, over 1 cm., so that the high speeds possible with this type of pump can be secured to advantage. An interior-cooler, which is provided in the upper half of the pump cylinder, effectively increases the area of condensation.

The two pumps are connected by steel tubing of $1\frac{1}{4}$ inch bore, the joints being made conveniently and quickly by the use of solder cups, which have been found to behave satisfactorily over a period of some months.

III. SPEED OF THE PUMP SYSTEM.

The speed of a vacuum pump has been defined by Gaede in the following way:—

If at any instant (t) the pressure in the vessel being exhausted is p , then

$$-\frac{dp}{dt} = kp,$$

where k is a constant over a limited range of p . Since the time taken for exhaustion varies inversely as V , the volume being exhausted, we can write

$$-\frac{dp}{dt} = \frac{S}{V} \cdot p,$$

or, on integration,

$$S = \frac{V}{t_2 - t_1} \log_e \frac{p_1}{p_2}.$$

If the vessel being exhausted is immediately adjacent to the pump, then S is the speed of the pump and is measured in c.c./sec. of gas at the pressure obtaining at the instant considered.

Determinations have been made as to the way in which S varies with the pressure for the metal-pump combination under discussion. The values were obtained by means of a constant flow apparatus, using Knudsen's¹² general equation

$$F = aP + b \frac{(1 + c_1 P)}{(1 + c_2 P)}$$

for the flow of a gas through tubing of circular cross-section. F is the flow in c.c./sec., measured at a pressure

of 1 dyne/cm.² for 1 dyne/cm.² pressure-difference between the ends of the tube; P is the average pressure in the tube in dynes/cm.², and a , b , c_1 , and c_2 are constants for a given tube when air is the gas considered.

The flow-tube employed connected two spherical bulbs of about 8 cm. diameter, one of which was joined to the low-pressure end of the pump system and the other was connected to the high-pressure end of the pump system through a drying-tube. In this way the pumps were used to circulate dry air through the flow-tube, without occasioning any flow to the supporting oil pump, so that the latter in no way contributed to the pump-speed measured by this method. The pressures in the bulbs were read, as soon as a steady state obtained, by means of two McLeod gauges connected one to each bulb. For pressures less than about 150 dynes/cm.² the flow-tube was 42 cm. long and 1 cm. diameter; for higher pressures the flow-tube was 36 cm. long and 0.5 cm. diameter. The connecting tubing between the low-pressure bulb and the pump system was 14 cm. long and 2.71 cm. diameter.

To consider the case of the flow-tube for the lower pressures, the flow Q * through the tube under a pressure-difference $(p_1 - p_2)$ is given by the equation

$$Q = F(p_1 - p_2) = \left\{ 3.24 P + 279.2 \frac{(1 + 0.1903 P)}{(1 + 0.2360 P)} \right\} (p_1 - p_2).$$

Also $Q = S'p_2$, where S' measures in c.c./sec. of air at pressure p_2 the pumping speed at pressure p_2 of the system comprising the pumps and connecting tube. The true pump speed S is obtained from this, as follows:—

If the pressure at the pump end of the connecting tube is p_3 , and F' is the flow through the tube for unit pressure-difference at its ends, then we have

$$Q = F'(p_2 - p_3) = S'p_2 = Sp_3,$$

or

$$\frac{1}{S} = \frac{1}{S'} - \frac{1}{F'}.$$

F' can be obtained from Knudsen's equation, being in this case

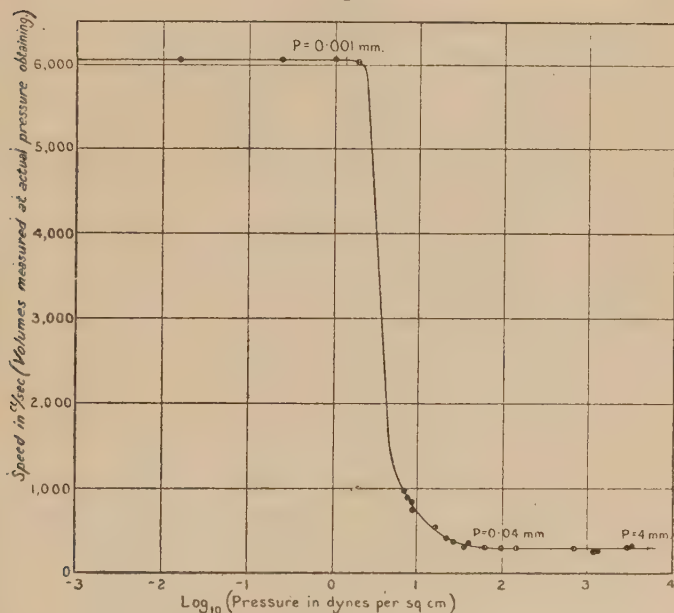
$$F' = 524 P' + 13730 \frac{(1 + 0.516 P')}{(1 + 0.639 P')}.$$

* Q is measured in c.c. per sec., the volume measurements being referred to a pressure of 1 dyne/cm.²

For low values of P' , F' is nearly constant, while for higher values $\frac{1}{F'}$ is very small compared with $\frac{1}{S'}$, so that P' may be taken as being equal to p_2 without making appreciable error.

In this way values of S have been found for various values of P' . In seeking a graphical representation of the results, it is more convenient and illuminating to plot S against $\log P'$, and this has been done in fig. 3. The graph

Fig. 3.



clearly shows that the speed of the pump system at pressures from 4 mm. to 0.03 mm. is constant and equal to 300 c.c./sec., this being due to the jet pump alone. Below this pressure the condensation pump begins to operate and the speed increases rapidly to 6000 cc./sec. at 0.0015 mm. pressure, and remains constant at this value for lower pressures. This may be regarded as a minimum figure which normally obtains without undue care as to the conditions. However, by careful adjustment of the temperature for any particular pressure, it has been found possible to increase this value to as much as 10,000 c.c./sec.

IV. ADVANTAGES OF THE PUMP SYSTEM.

The advantages of this type of two-stage pump system may be summarized as follows :—

- (1) The speed of pumping is extremely high.
- (2) Pressures of the order of 10^{-6} mm. or less (*i.e.* the lowest pressures obtainable by any type of pump) are possible when supported by a simple piston oil pump.
- (3) There are no moving parts, so that there is a complete absence of vibration, mechanical wear, and noise.
- (4) Vapours are pumped as efficiently as permanent gases.
- (5) No drying or other reagents are required.
- (6) The system is very robust and dependable since glasswork and rubber joints are eliminated.
- (7) The temperature control is not critical and the system requires little or no attention while running.
- (8) There is a continuous passage from supporting pump to high vacuum, so that no by-pass is necessary. The occurrence of a sudden leak in the apparatus under exhaustion or the failure of the supporting piston-pump will not occasion the overflow of liquid from the pumping system.
- (9) The running costs are low.
- (10) The weight is much less than that of the usual rotary oil-pump combination, so that the system is more readily portable when occasion demands.

SUMMARY.

A two-stage mercury-vapour pump system constructed wholly of steel has been devised, which consists of a jet-pump and a condensation-pump in series. The system requires a fore-vacuum of 4 mm. to afford the highest vacuum obtainable by a mercury condensation pump. There are no moving parts, vapours are pumped as efficiently as gases, no drying reagents are required, and glass work and rubber joints are eliminated. Above 0.03 mm. pressure the speed (using Gaede's definition) is constant at 300 c.c./sec.; below this pressure the speed increases rapidly to a constant value of 6000 c.c./sec.

A short resumé of existing vacuum pumps is given in this paper. The following approximate speeds are quoted :—

	c.c./sec.
Gaede rotary oil-pump	100–150
Gaede rotary mercury-pump ...	100
Gaede diffusion pump	100
Gaede molecular pump	1400 (max.)
Langmuir condensation pump ...	3000–4000

The all-metal pump system described in this paper, which has in the main been designed and tested by I. Backhurst, was made in the workshops of the National Physical Laboratory. Much help in the construction and testing of the pumps has been given by Mr. J. Balmanno and Mr. W. H. Sewell, of the Observer Staff of the Laboratory.

The investigation, which is being continued, has been carried out in part in connexion with work in progress for the Radio Research Board of the Department of Scientific and Industrial Research.

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In Glazebrook's 'Dictionary of Applied Physics,' vol. i. p. 24, a useful list of references will also be found.

XCI. *Geometrical Note on de Sitter's World.**By P. DU VAL **

THE Hyperbolic world of four dimensions is describable by means of Wierstrassian homogeneous coordinates x, y_1, y_2, y_3, y_4 ; a point is determined by the ratios of these, and for a real point the ratios are all real, so that if x is real all the coordinates are real. The manifold of real points is divided into three portions by means of the function $x^2 - \Sigma(y^2)$. Points for which—all the coordinates being real— $x^2 > \Sigma(y^2)$ are actual, those for which $x^2 = \Sigma(y^2)$ are absolute, those for which $x^2 < \Sigma(y^2)$ are ideal.

In discussing the actual field of this world, it is convenient to subject the coordinates to the condition $x^2 - \Sigma(y^2) = 1$. With this convention we find that the linear element ds between two infinitesimally neighbouring points is given by

$$ds^2 = \Sigma(dy^2) - dx^2.$$

For a discussion of the ideal field of this world it is manifestly more convenient to make our restriction $x^2 - \Sigma(y^2) = -1$. This is equivalent to multiplying by i each of the coordinates obtained by the former restriction; the infinitesimal increments of the coordinates are, of course, multiplied by i also, and the square of the linear element accordingly becomes

$$ds^2 = dx^2 - \Sigma(dy^2).$$

Since our five coordinates satisfy an equation, we can express them in terms of four parameters so that this equation becomes an identity. Let us put

$$\begin{aligned} x &= \cos \chi \sinh t, \\ y_1 &= \cos \chi \cosh t, \\ y_2 &= \sin \chi \cos \theta, \\ y_3 &= \sin \chi \sin \theta \cos \phi, \\ y_4 &= \sin \chi \sin \theta \sin \phi. \end{aligned}$$

Then $x^2 - \Sigma(y^2) = -1$ identically. To every set of values (t, χ, θ, ϕ) correspond determinate values of (x, y_1, y_2, y_3, y_4) , except where $\chi = \pm \frac{\pi}{2}$, $t = \pm \infty$ which give $y_1 = 0$, $x = 0 \times \infty$, and the ratios of y_2, y_3, y_4 determined by θ, ϕ . There are more cases in which (x, y_1, y_2, y_3, y_4) leave some of (t, χ, θ, ϕ) indeterminate; thus $y_3 = y_4 = 0$ makes $\theta = 0$, ϕ indeterminate;

* Communicated by the Author.

$y_2=y_3=y_4=0$ makes $\chi=0$, θ and ϕ both indeterminate ;

$x=y_1=0$ makes $\chi=\pm\frac{\pi}{2}$, t indeterminate.

In terms of (t, χ, θ, ϕ) the expression for the linear element becomes

$$ds^2 = \cos^2 \chi dt^2 - \{d\chi^2 + \sin^2 \chi (d\theta^2 + \sin^2 \theta d\phi^2)\}$$

which is the expression for the linear element in de Sitter's spherical world. Since a change in sign of all the Wierstrassian coordinates leaves them still referring to the same point, χ is indeterminate to the extent of an additive π , θ and t to the extent of a simultaneous additive π and $i\pi$ respectively. Thus it is the elliptic case, not the spherical, of de Sitter's world which is the ideal field of the Hyperbolic world.

The curve in the Hyperbolic world along which $\int ds$ between any two points is stationary for all infinitesimal deformations which vanish at the two end-points, is the straight line. Thus in de Sitter's world we can say that the world-line of a particle is a straight line. If the line joining two points A, B meet the absolute $x^2 = \Sigma(y^2)$ in I_1, I_2 , the distance $\overline{AB} = \frac{1}{2} \log R(ABI_1I_2)$; so that if I_1, I_2 are real distinct points \overline{AB} is real, if I_1, I_2 coincide $\overline{AB}=0$, if I_1, I_2 are conjugate complex points \overline{AB} is purely imaginary. That is, lines through any given point are either

- (i.) timelike, *i.e.* containing real intervals ; they are secants of the absolute ;
- (ii.) minimal, *i.e.* containing zero intervals between non-coincident points ; they are tangents of the absolute ;
- (iii.) spacelike, *i.e.* containing purely imaginary intervals between real points ; they are non-secants of the absolute.

The whole world cannot be described by real values of (t, θ, ϕ, χ) . We may take any timelike straight line as $y_2=y_3=y_4=0$, *i.e.* as the world-line of an observer who considers himself permanently at rest at the origin of elliptic-polar coordinates (χ, θ, ϕ) in space. We find that $t=s$ along this line ; and that every partition $t = \text{const.}$ is perpendicular to this. Also, since

$$x \cosh t = y_1 \sinh t,$$

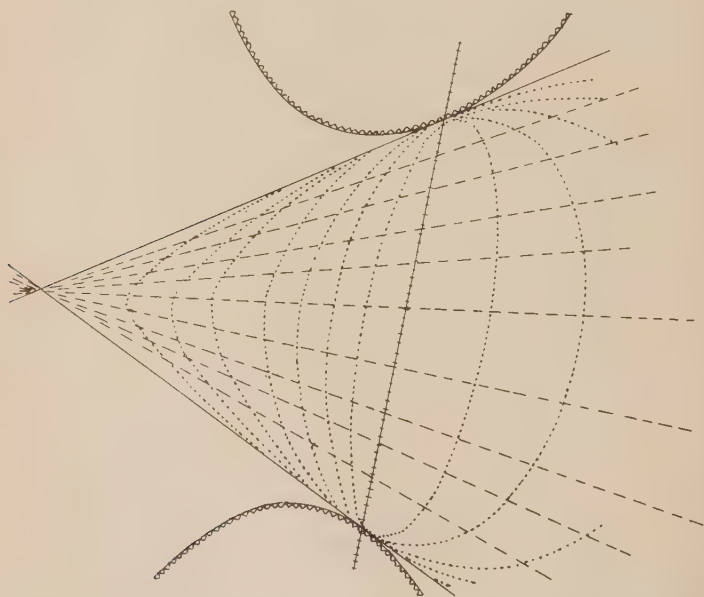
$t = \text{const.}$ is a flat space, *i.e.* one which if it contains two points of a straight line contains the whole of it. These

spaces all intersect in the horizon, $x=y_1=0$, which is the polar plane of $y_2=y_3=y_4=0$. Now the tangent spaces to the absolute at its intersections with $y_2=y_3=y_4=0$ meet in this polar plane, and are thus the spaces which join the plane $x=y_1=0$ respectively to the points $(y_2=y_3=y_4=0, x-y_1=0)$ and $(y_2=y_3=y_4=0, x+y_1=0)$ respectively. These two points are $t=\pm\infty$ at the origin of space. But we have seen that the space joining $x=y_1=0$ to the point $t=t_1$ at the origin of space, is the locus $t=t_1$; thus the loci $t=\pm\infty$ are the tangent planes to the absolute at its intersections with $y_2=y_3=y_4=0$. The locus $\chi=\text{const.}$ is given by

$$x^2-y_1^2=\cos^2\chi(x^2-\Sigma(y^2));$$

this is a quadric which meets the absolute in the same surface as does the locus $x^2-y_1^2=0$, or $t=\pm\infty$, which we have seen

Fig. 1.



to consist of two flat spaces, both touching the absolute. Thus the surface of intersection reduces to two conjugate points—the points of tangency. Thus $\chi=\text{const.}$ is an equidistant-locus whose axis is the line joining these two points of tangency, *i. e.* $y_2=y_3=y_4=0$.

Fig. 1 represents a plane section of the world, given by determinate values of θ, ϕ , in the Cayley-Klein projection. The absolute is shown by ~~~~~, the world-line of the

origin by +++++, the loci $t = \pm \infty$ by ———, other time partitions by ———, and the space partitions $\chi = \text{const.}$ by The plane meets the "horizon" in a point in which the traces of all the time partitions are concurrent.

The motion of a particle in this space is very simple—its world-line is a straight line. Now the equations of a straight line are

$$y_2 = A_1 y_1 + A_2 x,$$

$$y_3 = B_1 y_1 + B_2 x,$$

$$y_4 = C_1 y_1 + C_2 x,$$

$$i. e., \quad \tan \chi \cos \theta = A_1 \cosh t + A_2 \sinh t,$$

$$\tan \chi \sin \theta \cos \phi = B_1 \cosh t + B_2 \sinh t,$$

$$\tan \chi \sin \theta \sin \phi = C_1 \cosh t + C_2 \sinh t.$$

If the motion is restricted to be radial, *i. e.* if θ, ϕ have fixed values, we have

$$\tan \chi = A_1 \cosh t + A_2 \sinh t.$$

There are three cases of this; if $|A_1| > |A_2|$, the equation becomes

$$\tan \chi = A \cosh (t - t_0),$$

showing that the particle approaches the origin with negative acceleration till it reaches a minimum distance $\tan^{-1} A$ at time t_0 , after which it recedes. If $|A_1| < |A_2|$, we have

$$\tan \chi = A \sinh (t - t_0).$$

Here the particle approaches the origin, passes through it with minimum velocity $\frac{dx}{dt} = A$, and recedes on the other side. The limiting case

$$\tan \chi = A (\cosh t \pm \sinh t)$$

gives a particle which recedes from or approaches the origin asymptotically.

These three cases are those in which the world-lines of the origin and the moving particle intersect in the actual field, the ideal field, and the absolute respectively.

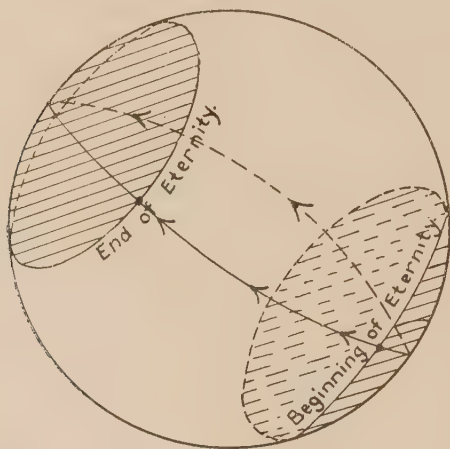
In the elliptic case, which is what most naturally arises from consideration of Hyperbolic Geometry, the absolute is a single closed curve, and every timelike line meets it in two points. There does not seem to be any particular way in which we can discriminate between $t = -\infty$ and $t = +\infty$ for an observer whose body is in that line. Certainly every observer has a consciousness which works in a definite sense along his world-line, being at every point of his life conscious

of events in the line on the negative side of him, but not on the positive side. Moreover, the light-cone (*i. e.* the cone of minimal lines) at whose vertex he is, is divided there into two sheets, the fore-cone and the after-cone, and he can see the events of the first sheet and not those of the second.

How is this clearly marked sense determined? It is absurd to suppose that each observer's sense is determined at random, for it is certain that the entire human race—whose lines are sensibly parallel—are set the same way along them.

In the spherical case this difficulty vanishes. Here the absolute consists of two distinct closed curves, which separate two distinct actual fields from an annular ideal field. The state of affairs may best be shown on a spherical surface, representing straight lines by great circles, and the absolute

Fig. 2.

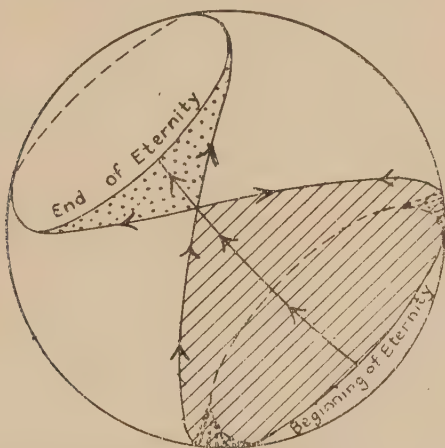


by the two branches of a spheroconic. In fig. 2 the actual fields are shaded. Every timelike line now has two actual and two ideal segments; each actual segment is bounded by two points on the same branch of the absolute, but each ideal segment is bounded by one point on each branch. The two ideal segments, being wholly distinct, are the tracks of different particles; and we may regard a world-line as consisting of one ideal segment only; with this convention we see that every world-line meets each branch of the absolute once; so that we can make the condition that all points $s = -\infty$ (s = proper-time along a world-line) lie on one branch, the beginning of eternity, and all points $s = +\infty$ on the other, the end of eternity.

Thus the phenomenon of memory may be roughly summarized by saying that an observer has some consciousness of events in his world-line between himself and the beginning of eternity, none of events on the other side of him.

A line which touches the beginning touches also the end of eternity; this is a minimal line or light-track; the two points of tangency divide it into two segments; and we must suppose light starts at the $-\infty$ point, and travels along the line both ways to the $+\infty$ point. Thus a single segment constitutes a light-track. In fig. 3 two light-tracks are shown intersecting at a point in the observer's life, which divides each of them into a fore-cone segment and an after-cone segment. The

Fig. 3.

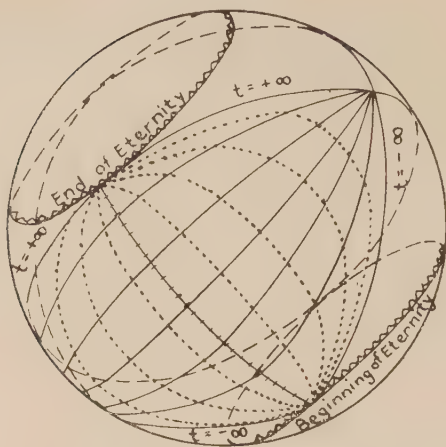


shaded area represents the events which he can see, or has already seen; the dotted, world-points from which he is visible, or will yet be visible.

Fig. 4 represents the same as fig. 1. The absolute is shown by $\sim\sim\sim\sim$, the world-line of the observer by $|||$, the time partitions by $---$, and the space partitions by $\dots\dots\dots$. The horizon plane now meets the plane of section in two antipodal points, $\chi = +\frac{\pi}{2}$ and $\chi = -\frac{\pi}{2}$ for the given values of (θ, ϕ) .

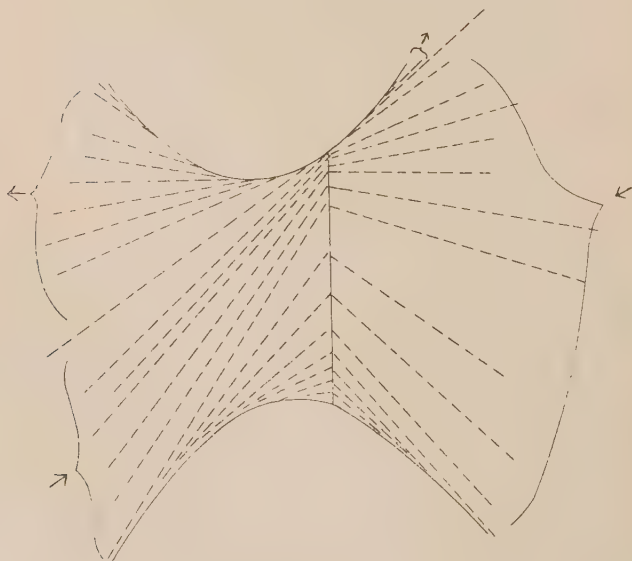
Another question of interest is, how much of the world does the observer see at one time and another during eternity? In the elliptic world he sees all of it, in the spherical world half. The same is true of the portion of the world from

Fig. 4.



which one event or another in his world-line can be seen. Fig. 5 illustrates the elliptic case in the Cayley-Klein representation.

Fig. 5.

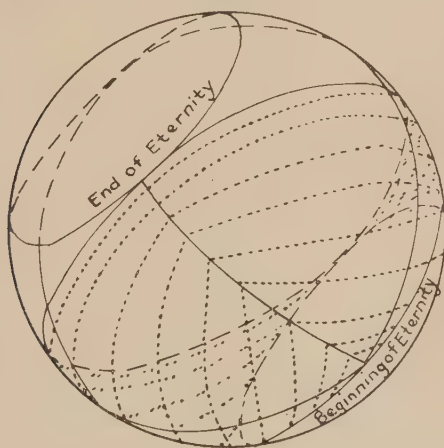


From this figure (which shows the fore-cone only, at various points of the world-line) it appears that in the elliptic world the sense in which light travels in a minimal

line is relative to the observer, *i. e.* there is no absolute distinction between fore-cone and after-cone; the observer merely, having his consciousness turned in some obscure way towards his past, sees that part of the cone which lies on the same side of him as his past. This relativity is made evident by the abrupt change in sense of the light, which occurs at the minimal $t = +\infty$. If the corresponding figure be drawn for the after-cones, it is evident that some point in the world-line is visible from everywhere in the world, and that a further discontinuity of sense in the light rays occurs at $t = -\infty$.

The spherical case is illustrated in fig. 6. The fore-cones are shown by , the absolute, the world-line, and the

Fig. 6.



minimals $t = \pm\infty$ by ——. The region covered by the fore-cones includes the coordinate field, and the two spandril-shaped regions between $t = \pm\infty$ and the beginning of eternity. Similarly, the region of the after-cones includes the coordinate field, and the other two spandrils, between $t = \pm\infty$ and the end of eternity. The field antipodal to the coordinate field is not included in either region. This field, as a matter of fact, is also described by real (t, χ, θ, ϕ) , since the antipode of (t, χ, θ, ϕ) is $(t, \chi + \pi, \theta, \phi)$. It is, however, separated from the ordinary coordinate field by the horizon, and no point in the one field is visible from any point in the other, except those of the loci $t = \pm\infty$. These two loci, as well as being flat spaces, are also pencils of light-rays; thus

light-rays diverge from $(t = -\infty, \chi = 0)$, in every direction in the space $t = -\infty$; each ray passes through a point in the horizon, and they converge to the point antipodal to $(t = -\infty, \chi = 0)$. Similarly, rays converge on $(t = +\infty, \chi = 0)$, which have all started from the antipodal point and come through the horizon. It is thus a little misleading to assert that light is arrested at the horizon. The analytical results which appear to suggest this are really expressions of the singularities which occur in the transformation from (t, χ, θ, ϕ) to (x, y_1, y_2, y_3, y_4) .

We have here two worlds to choose from as approximate representations of phenomena.

The spherical world offers a possible definition of past and future sense on a timelike world-line. On the other hand, half only of the world can come within the experience, either direct or visual, of any one observer; and it is a little problematic how far we can with meaning assert the existence of the other half.

The elliptic world has the advantage that it affords a concise description of just what is visible to one observer of infinite longevity; but it leaves to chance the discrimination between his past and his future. One would certainly be inclined to say that there was an *a priori* distinction between the two senses of time; but we must remember that our conviction of this can only refer to the earth, or at least the solar system. We have really no means of knowing that inhabitants of Sirius have not memories and eyes that work the opposite way to ours; or indeed that their memories and eyes do not work both ways at once, so that the fore-cone and after-cone have no different properties for them. As for the solar system, of course, the irregular local departures from de Sitter's metric which constitute the matter of it may be such as to bind all the particles of it together in a way that leaves sameness of sense between the world-lines of two of them definable. Thus the elliptic case is not inconceivable; and it is certainly more amusing than the spherical. The possibility—remote, it is true—of the entry into our world of someone whose memory works backwards, is to me a sufficient reason for believing in elliptic, not spherical, geometry; not to mention that projective geometry is so much simpler when two straight lines cannot meet in more than one point.

XCII. *Note on the Wave Form of the Current when an Electric Discharge is passed through Mercury Vapour.* By F. H. NEWMAN, D.Sc., A.R.C.S., Professor of Physics, University College, Exeter*.

[Plate VII.]

IT has been noticed by Pierce† that the Cooper Hewitt mercury vapour lamp will under certain conditions act as a low resistance air-gap but with greater uniformity. If the terminals of such a lamp are shunted by a condenser in series with an inductance, and a high voltage is applied to the terminals, electrical oscillations are excited in the condenser circuit which includes the condenser, inductance, and mercury lamp. As the voltage increases the condenser becomes charged, but the mercury vapour when cold is a non-conductor. At a certain voltage the resistance of the mercury vapour, due to the disappearance of the cathode resistance, breaks down, and a current passes through it. The condenser discharges through the lamp with oscillations providing that $\frac{L}{C}$ is greater than $\frac{R^2}{4}$ where L is the self-induction, C the capacity, and R the resistance of the circuit. When the voltage falls to a critical value the mercury vapour ceases to conduct and maintains its high resistance until the voltage rises again, and the process is repeated. Because of this high initial resistance about 5000 volts alternating current is required to maintain a current of about two amperes through the lamp, whereas 100 volts continuous current is sufficient to maintain the arc.

The lamp acts like a spark-gap in air, but with greater regularity. Pierce found that several discharges may occur during a single half-cycle of the transformer, the number increasing with decrease of capacity. Thus with 15,000 volts and a capacity of 0.117 microfarad he found that one or two discharges per half-cycle were obtained, while with a small capacity and the same voltage, over 200 complete discharges per half-cycle were obtained. The recovery is thus very rapid. The discharge of the condenser was never complete, the residual voltage being sometimes positive and sometimes negative. The resistance of the interrupter decreased with increasing capacity of the condenser and with decreasing inductance.

It was found during some experiments on the electric discharge through mercury vapour, that results somewhat similar to those described above were obtained. The

* Communicated by the Author.

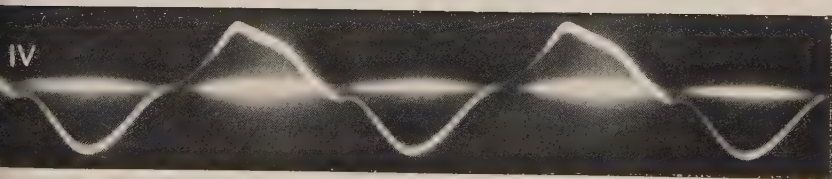
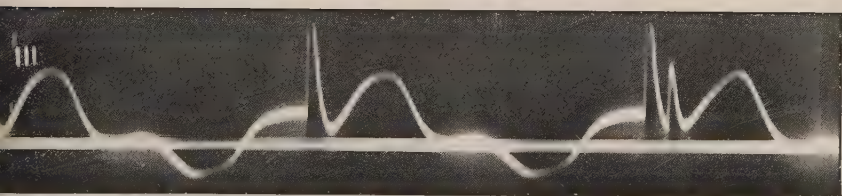
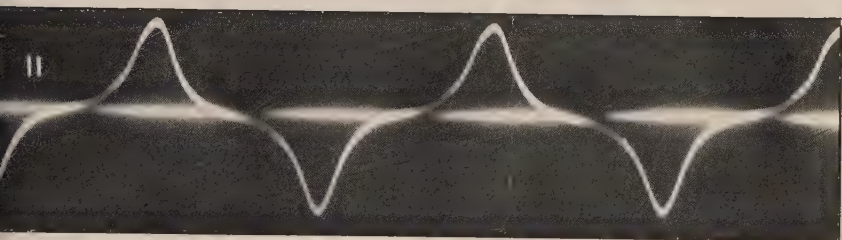
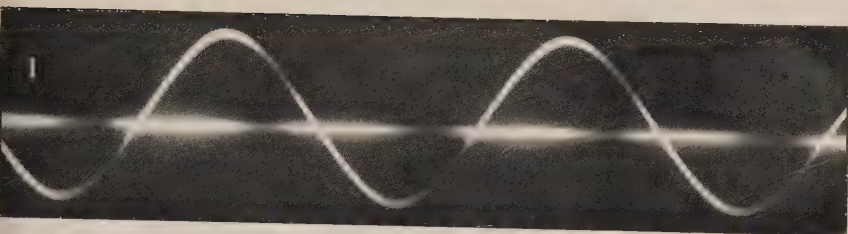
† Proc. Amer. Acad. of Science, xxxix. (1904).

discharge tube was a bulb about 12 cm. diameter, with two pools of mercury forming the electrodes ; the surface area of the two electrodes was different. The secondary of a transformer was connected to the electrodes, and an alternating current of period 60 per sec. and voltage 20,000 volts was sent through the discharge tube. A Duddell oscillograph was connected in series, and the current passing through the bulb was sufficient to cause a suitable deflexion of the vibrating mirror. The fibre in the oscillograph was so stretched that it was able to follow any variations in the current up to about 300 per sec.

When the discharge was passed without any self-induction or capacity in shunt with the tube, the wave form of the current was practically symmetrical and a sine curve. The addition of self-induction as a shunt caused each half-cycle of the discharge to become asymmetrical, *i. e.* the current increased at a slower rate, with an increasing voltage, than its rate of decrease after reaching its maximum value. The wave form was no longer a sine curve but became peaked at the maximum. The substitution of a capacity for the inductance in the shunt circuit altered completely the form of the discharge, as is well shown in Plate VII. (III.). With increasing voltage the condenser is charged and no current passes through the mercury vapour. At a certain critical voltage the condenser discharges with oscillations through the tube ; in the case shown two discharges were obtained, although owing to the applied voltage the condenser never completely discharged. This oscillatory discharge of the condenser only occurred during one half of the alternating voltage cycle. The wave form of the discharge during the succeeding half-cycle differed entirely and showed no oscillations. This asymmetry is due to the resistance of the discharge-tube depending on the direction of the current with electrodes of different surface areas. The amplitude of the current during one half-cycle was greater than that in the succeeding half-cycle.

Combining a suitable self-inductance with a capacity in shunt with the tube caused a unidirectional discharge of the condenser. This is illustrated in Plate VII. (IV.). In this case $\frac{R^2}{4}$ is greater than $\frac{L}{C}$. The discharge shows asymmetry in one half-cycle, and also the wave form depends on the direction of the current through the tube.

The oscillograms show that the addition of a capacity as a shunt to the electric discharge-tube increases the "peak" value of the current through the tube.



- I. No capacity or inductance in shunt.
- II. Inductance 0.42 henry in shunt.
- III. Capacity 0.09 microfarad in shunt.
- IV. Capacity 0.04 microfarad, inductance 0.62 henry in shunt.

XCIH. *On the Critical Frequency of Pulsation of Tones.* By
FRANK ALLEN, *Ph.D., Professor of Physics, University of
Manitoba, Winnipeg, Canada* *.

IN a recent communication with the above title to the Philosophical Magazine †, several relationships were deduced from the experimental data connecting D, the duration of a pulse of sound at the critical frequency of pulsation or flutter of a tone, P, the blowing pressure of the air in the tonvariator, to which the intensity of the sound is proportional, and N, the frequency of vibration of the tone.

The most important of these relationships is that connecting D and P, and was given in the paper:

$$D = K \sqrt{\log P} + C,$$

where K and C are constants.

This equation, applied to the experimental measurements contained in Table II. in the former paper, gave a series of straight lines for different values of N, which were shown in fig. 3, p. 56, in the paper. The lines were so uniformly straight that it was concluded this equation completely satisfied the experimental data.

TABLE.

Pressure P.	log P.	D. N=170. sec.	D. N=180. sec.	D. N=200. sec.	D. N=240. sec.	D. N=264. sec.
2.40 cm.	.380	0.0203	0.0198	0.0189	0.0172	0.0164
2.20 „	.342	.0200	.0196	.0186	.0170	.0160
2.10 „	.322	.0197	.0192	.0183	.0166	.0157
1.98 „	.297	.0194	.0189	.0179	.0162	.0154
1.82 „	.260	.0191	.0186	.0176	.0160	.0151
1.70 „	.230	.0189	.0184	.0173	.0156	.0147
1.62 „	.209	.0186	.0181	.0171	.0153	.0144
1.53 „	.185	.0182	.0177	.0167	.0150	.0141
1.45 „	.161	.0177	.0172	.0162	.0143	.0134
1.25 „	.097	.0168	.0163	.0153	.0135	.0126

Reference was also made in the paper to the analogous

* Communicated by the Author.

† Vol. xlvii. p. 50 (1924).

equation of T. C. Porter, connecting D , the duration of a flash of light at the critical frequency of flicker, and L , the intensity of illumination of a black and white disk,

$$n = \frac{1}{D} = K \log L + C.$$

This equation, when applied to Porter's measurements on white light, was found to have two values for the constant, K , and therefore represented two straight lines with different inclinations, which met at a point representing the low illumination of 0.25 metre-candle.

As this peculiarity of Porter's law has been interpreted as applying to vision by the rods for dim light, and by the cones for bright, there seemed to be no reason why a similar phenomenon should occur in the perception of sound, since nothing suggestive of a double percipient mechanism corresponding to rods and cones exists in the ear.

The authors therefore felt satisfied that the square root of $\log P$ was involved in the sound measurements, and did not discover the direct relationship which is here shown to exist.

Recent unpublished work in the writer's laboratory on the sense of touch has brought to light a phenomenon of double action precisely similar to Porter's law in the visual sensation. In consequence of this discovery, the data on sound were re-examined in order to see if Porter's law held there within the range of intensities studied. On plotting the values of D , from Table II. referred to above, and $\log P$, each of the curves was found to consist of two straight lines similar to those found by Porter.

These are shown in the new figure in this paper. Each pair of lines represents observations made on a tone of the frequency indicated, when it was varied from the lowest to the highest available intensity. It may be remarked that Ives* found Porter's law to apply to each spectral colour with a suitable change in the constants. This was confirmed by the writer†.

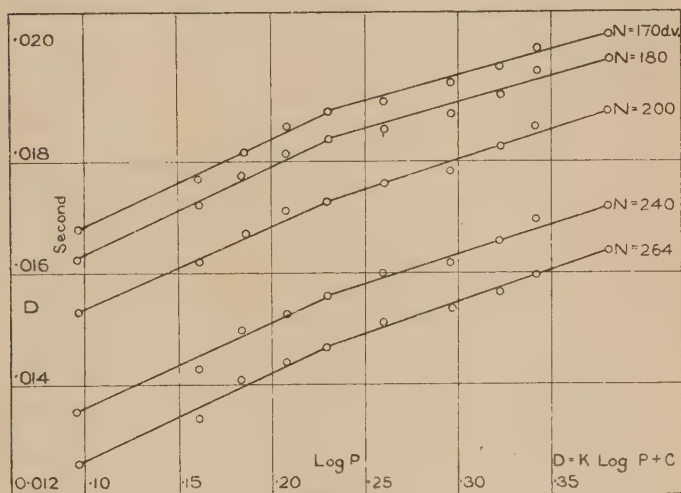
Table II. of the former paper is given here together with the values of $\log P$ instead of the square root of that quantity.

* Phil. Mag. vol. xxiv. p. 358 (1912).

† Phil. Mag. vol. xxxviii. p. 81 (1919).

The change in slope of the lines in the figure occurs in each case at an intensity given by the tonvariator when blown by an air-pressure of 1.70 cm. of water. This is a quite weak sound, and is comparable with the position of the analogous point found by Porter at the intensity of 0.25 metre-candle.

In the former paper it was pointed out that Porter's law requires the reciprocal of D , whereas in sound D appears directly.



Porter found the angle of inclination made by the upper line representing high intensities to be nearly twice that of the lower. Inserting the numerical values of the constants, Porter's law may be written

$$n = 12.4 \log L + 10, \text{ for high intensities,}$$

and

$$n = 1.56 \log L + 17.75, \text{ for low intensities.}$$

The lower branches of the curves for sound in the figure are practically parallel, with a mean angle of inclination of $24^{\circ} 52'$. The upper branches, for more intense sounds, slightly converge, that for $N = 170$ d.v. having an angle of 15° and the others successively, 16° , $17^{\circ} 30'$, $17^{\circ} 45'$, and $18^{\circ} 30'$. In the analogous case of colours Ives found a similar convergence of the lines.

Porter's equations applied to sound may be written

$$D=0.01558 \log P + C, \text{ for low intensities}$$

and

$$D=0.01027 \log P + C, \text{ for high intensities,}$$

where 0.01027 is the mean value of the five constants, which range from 0.00932 to 0.01134.

The values of C vary for the different curves, and apparently are not physiologically significant, unless possibly they may have some connexion with threshold values. It will be noticed also that the larger value of the constant, K , in Porter's equations is for high intensities, whereas the opposite is the case with sounds.

Since Porter's law is derived from Fechner's law*, which is fundamental in sensory nerve action, it ought, therefore, to follow that the fundamental sensory actions and reactions should be similar with all the sense organs. The peculiar alteration of direction of the lines when changing from weak light to strong ought also to be found when changing from any weak sensory impressions to strong. This we now find to be the case with the sensations of sound and touch in addition to that of light.

In light, the Porter effect, as we may conveniently term it, has been referred to the change from rod vision to cone, and therefore has been regarded as confirmatory of the Duplicity Theory of Vision of von Kries. But from the additional evidence adduced here, such an interpretation becomes extremely improbable. The Porter effect appears to be a general property of the sensory nervous system, and hence must be referred to some fundamental property that all such nerves possess in common. The most probable location of the effect appears to the writer to be in the synapses, which Sherrington has found to possess a large number of important functions in nerve conduction.

As it is the intention of the writer to discuss this subject more fully when the experimental data now accumulating are complete, only this addition to, and correction of, the former paper, and its most obvious implications, are noted at present.

On p. 56 of the paper referred to the value .0311 in Table II. should be .311, and on p. 57 the word "arbitrary" should be omitted from the last line, as the constants are determined by the nature of the phenomenon and by the mode of experimentation.

* Peddie, 'Colour Vision,' p. 162.

XCIV. *The Non-Metallic Elements. Connections between their Dielectric and other Physical Properties.* By G. L. ADDENBROOKE*.

BOLTZMANN, in 1873, described a method of obtaining dielectric constants by observation of the attraction of a small sphere of a dielectric hung near a large charged sphere, as compared with the attraction of a similar small metal sphere taken as a standard.

There is a full description of this work, with a memoir specially written by Boltzmann himself, in Gordon's 'Electricity and Magnetism.' See also Poynting and Thomson's 'Electricity and Magnetism,' 1914.

The pulls found were connected with Dielectric Constants (K) by the equation :

$$\frac{\text{Pull on dielectric sphere}}{\text{Pull on metal sphere}} = \frac{K-1}{K+2}$$

It is noteworthy that Boltzmann arrived at this relation by purely electrical reasoning, the steps of which are given by Gordon.

Boltzmann first found the dielectric constants of four different substances by putting plates of them between two electrodes.

He then found their dielectric constants by his attraction method and showed that the results were practically identical. The work was afterwards extended by his pupils over a wider range of dielectrics. Boltzmann's formula thus shows the connexion between two quantities, each of which can be measured directly and separately.

In the limiting case of a parallel or symmetrical field, the two electrical opposite pulls on the dielectric are equal, and therefore there is no movement of the dielectric as a whole; but taking two vertical plates as electrodes, Thornton (Proc. Royal Soc. A, vol. lxxxii., 1905) hung a thin ellipsoid of a dielectric centrally between them and thus in a symmetrical field, the long axis perpendicular to the plates. On charging the two plates oppositely there is no movement, but if the ellipsoid is slightly rotated axially by momentarily twisting the suspension, its period of oscillation is longer when there is no electric field than when the field is charged. Thornton showed by a large number of experiments that, from the difference in time of the swings, dielectric constants can be obtained agreeing with those found by ordinary methods.

* Communicated by the Author.

In Boltzmann's arrangement the dielectric is bodily drawn towards the stronger field. In Thornton's, where the field is symmetrical, if the ellipsoid is rotated, the lines of force running partly through it are lengthened, and the two opposite pulls produce a restoring torque owing to the lines of force tending to shorten themselves.

While, for longitudinal movement of the dielectric, divergence or want of symmetry of the field is thus necessary, it is interesting and important to note what a small divergence is needed to get a substantial pull.

In the description of Boltzmann's work mentioned above, all the data and dimensions used are given. Assuming that the divergent field radiates from the centre of the charged sphere, the solid angle subtended between this point and a vertical section through the centre of the attracted dielectric sphere was under 10° . Again, I have set up a working model of Boltzmann's arrangements, but using a fine metallic strip suspension instead of his bifilar suspension with the threads at a considerable angle. Working on modern lines, it is clear that far greater sensitiveness can be obtained, and that, with potentials on the inducing sphere such as Boltzmann used, readable deflexions could be obtained at several times the distance at which he worked, and thus the angle of divergence of the field could be reduced to 2° or 3° . The extension of Boltzmann's reasoning to symmetrical fields where the two opposite pulls equalize each other is therefore a short step.

Converse Use of Boltzmann's Formula.

Consequently, if we know the value of K for a dielectric, as found by any recognized method, by placing this value in the above equation we can get the relative attraction of a sphere of a dielectric placed in a standard electric field, the attraction of an equivalent metal sphere being taken as unity.

The substantial nature of these attractions does not seem to be generally recognized.

For instance, in the Phil. Mag. for March 1923 there was a communication by me on the "Properties of a Flint Glass of Density 6," which had a dielectric constant of 13.

Taking the attraction on an equivalent metal sphere as unity, we get for the attraction in this case :

$$\frac{\text{Pull on dielectric}}{1} = \frac{13-1}{13+2} = \frac{12}{15} = \cdot 8;$$

that is, the pull on a sphere of this dielectric in an electric

field would be eight-tenths of that on a metal sphere of the same size. Similarly the pull on a sulphur sphere of $K=4$ is $\cdot 5$, and that on a paraffin sphere of about $K=2$ is $\cdot 25$. These facts are worthy of the serious attention of physicists studying the now accepted view of the nature of the atom.

Consideration of the Two Actions taking place when a Dielectric is placed in an Electric Field.

Consequently, when a dielectric is placed in an electric field and the potential difference is maintained constant from an outside source there are two measurable actions:—

(1) Ordinary capacity, or the electric storage action, the energy stored corresponding to $\frac{1}{2}QV$, or the quantity stored multiplied by half the potential difference.

(2) The actual pull on the dielectric, as explained above.

If a condenser with nothing between the plates except the æther is charged, a certain storage of energy takes place. If, then, a dielectric is inserted there is an additional storage of energy. The initial charge plus this additional charge divided by the initial charge is called the "dielectric constant," usually denoted by K . The question then is: Does the original storage of energy in the field disappear after the dielectric is inserted and become part of the energy stored in the molecules of the dielectric, or does it still exist as a separate entity? (See Drude's 'Optics,' p. 387.)

The modern view of the atom has now obtained general assent. A dielectric, therefore, consists of minute opposite point charges occupying a nominal space in the included æther, and the view is strengthened that, when a dielectric is inserted in an electric field—if the potential slope is maintained from an outside source—the storage of energy between the boundaries of the field is not appreciably altered, but that there is an additional and separate storage in the action which arises between the charges of the nuclei and electrons of the atoms of the dielectric and those of the electrodes which give rise to the field.

In a communication to the Phil. Mag. for March 1922, on a "Study of Franklin's Experiment on the Leyden Jar," I showed that, contrary to what is often taught, the action of an electric field on a dielectric is purely inductive, and that the charge disappears entirely when the field is removed, apart from any absorption. Absorption with good

dielectrics is small or negligible, in comparison with the instantaneous charge, for charges at ordinary alternating frequencies, though it may be a large factor if the time of charge is relatively long. Absorption can, however, be distinguished from instantaneous charge, as it is always accompanied by losses of corresponding magnitude, which can be separately measured with alternating fields by the electrostatic wattmeter and otherwise (see above communication, *Phil. Mag.* March 1923).

In this paper, therefore, the value of the additional action corresponding to $(K-1)$ is alone taken as a basis for comparing the relative amounts of energy stored by different dielectrics in given electric fields, and also for comparisons of the energy stored with the corresponding attractions; it will be called the "reversible energy storage equivalent," or "dielectric equivalent," a quantity which is less abstract than the term "dielectric constant."

Looking at Boltzmann's formula, it will be seen that it is also based on $(K-1)$ and not K .

There are, therefore, two separate actions which we can measure by putting dielectrics in electric fields:

- (1) The additional reversible energy storage corresponding to $(K-1)$;
- (2) The attraction, pull or stress measured directly and corresponding to

$$\frac{K-1}{(K-1)+3} \text{ or } \frac{K-1}{K+2}.$$

Relation of Attraction to Energy Reversibly Stored.

If a series of values of energy reversibly stored is plotted in a diagram corresponding to different values of K , or $(K-1)$, a rising straight line is obviously obtained.

If the corresponding attractions for the same range of values of K are plotted, the result is a curve.

Consequently, if relative values of energy reversibly stored and the corresponding attractions are compared over more than short ranges, considerable differences appear, as will be shown more fully later.

It therefore seemed desirable to have separate data for these attractions, also that comparisons of electric with other physical actions should not be based solely on K , or the energy stored in the dielectric plus that stored in the field, as is usually the case now, or even on $(K-1)$ alone.

Necessity of Using Atomic Values for Comparisons.

Since Faraday's time, however, it has been accepted that the action of an electric field on dielectrics is on their molecules. To make proper comparisons of the molecular attractions, or of their corresponding dielectric equivalents ($K_m - 1$), or reversible energy storage values, measurements must therefore be made of both actions on the same number of molecules in all cases.

Method of Obtaining Molecular Values of $K - 1$.

To obtain the molecular dielectric equivalents, or ($K_m - 1$) of dielectrics, we can proceed as follows:—

The number of molecules in a standard volume of any dielectric is proportional to the atomic volume of the substance, *i. e.*,

$$\frac{\text{Atomic weight}}{\text{Density}} = \text{Atomic volume.}$$

If, then, we write

$$(K - 1) \times \frac{AW}{D} = K_m - 1,$$

we get numbers which are proportionate to the values of the energy reversibly stored molecularly in different dielectrics, the procedure being similar to one which is frequently used by optical workers substituting N or N^2 for K .

But, while this is sufficient for getting a set of relative values of ($K_m - 1$) or of the energy reversibly stored, to get the relative molecular attractions we must have not relative, but actual, magnitudes for K_m . These values could be found experimentally if spheres were taken, the respective volumes of which were proportionate to the atomic volumes of the substances. We should then get spheres of different sizes and weights, the attractions of which would have to be compared with the attraction of a standard metal sphere. The same results could also be obtained by measuring the capacities of dielectrics between flat plates a standard distance apart, but varying the area of the plates to correspond with the atomic volume of the different dielectrics. The values can, however, be obtained with close approximation by calculation.

Application to Data for Elements.

What has been said above is of a general character, and is applicable to dielectrics of whatever nature. In this communication it is proposed to apply the conclusions

reached only to a study of the electric properties of certain elements.

The dielectric constants are now available for ten elements, including liquefied elementary gases, and investigations by the writer on absorption in dielectrics lead to the conclusion that the accepted dielectric constants of these elements (see Table I.), taken from the 1913 Tables of the French Physical Society, although not free from small observational errors and small differences due to absorption, are, nevertheless, sufficiently accurate to form a fair basis for considering the dielectric properties of these elements.

TABLE I.
Properties of Non-metallic Elements.

Element.	Atomic Weight.	Density.	$\frac{AW}{D} =$ Atomic Vol.	K. Dielectric Constant.
Hydrogen, Liquid	1	·071	14·1	1·21
Nitrogen, Liquid	14	·88	16	1·45
Oxygen, Liquid	16	1·25	12·8	1·47
Chlorine, Liquid	35·5	1·5	23·6	1·97
Bromine, Liquid	80	3·2	25	3·10
Iodine, Solid	127	4·66	27	4·00
Phosphorus	31	1·84	16·8	3·85
Sulphur	32	2·0	16	4·00
Selenium	79	4·28	18·3	6·14
Carbon	12	3·5	3·4	5·5

By referring to the above list, it will be seen that the atomic volumes of the three halogens are the largest, and also that they are nearly equal and cover an important and considerable range of the attraction curve. If, then, we make the atomic volume of one of them, say chlorine A.V. 23·6, our standard, the $(K_m - 1)$, or molecular $(K - 1)$, will be the same as that of the element in its natural (liquid) state, and this will also be nearly true for the other two halogens, bromine and iodine, which will therefore come in their right places.

If, then, we divide the relative values for all the elements by the atomic volume of chlorine, we shall get closely correct values of the corresponding molecular dielectric equivalents, or $(K_m - 1)$, and correct magnitudes for subsequent insertion in Boltzmann's formula, $\frac{K_m - 1}{K_m + 2}$ as used for finding the relative attractions.

The molecular values for $(K_m - 1)$ are given in Table II., column 2.

TABLE II.

Molecular Dielectric Equivalents of Elements, Actual and Comparative, on the Basis of the Natural Number of Molecules in Chlorine.

Element.	2.	3.	4.
	Actual Values of $K_m - 1$, or Energy stored.	Relative Values of $K - 1$, or Energy stored.	Relative Values, $\frac{K_m - 1}{K_m + 2}$, Attractions.
Hydrogen	·126	1·0	1·0
Nitrogen	·30	2·4	2·27
Oxygen	·256	2·02	1·98
Carbon	·65	5·2	4·5
Chlorine	·97	7·7	6·1
Bromine	2·22	17·8	10·5
Iodine	3·4	27·7	13·3
Phosphorus	2·0	16·2	10·0
Sulphur	2·04	16·2	10·1
Selenium	4·28	32·2	14·25

Inspection shows that the lowest value of $(K_m - 1)$ thus obtained is that for liquid hydrogen. Taking this as unity, all the other values are divided by it. We thus get a table of the comparative values of the energy reversibly stored in an electric field of standard potential slope for the elements here considered (see column 3, Table II.).

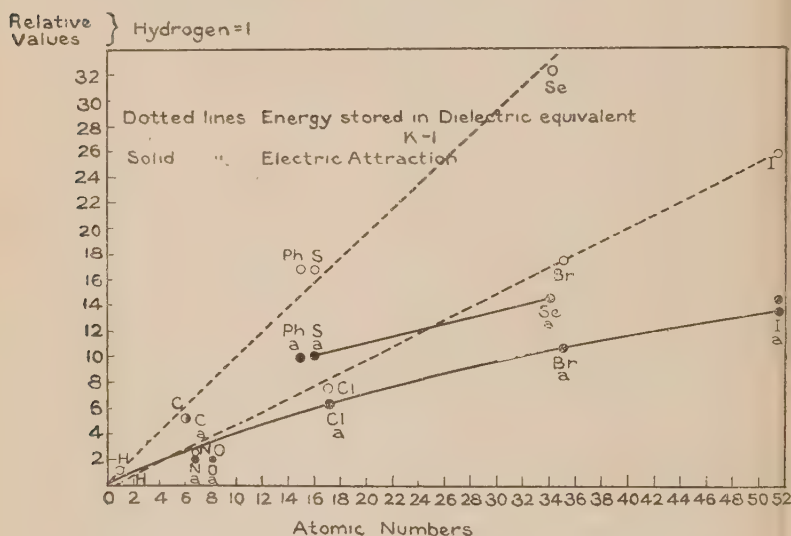
The corresponding relative values of the molecular electric attractions are given in column 4 of Table II. These are found by taking the values in column 1 and placing them in the equation $\frac{K - 1}{K + 2}$, and then taking the value found for hydrogen as unity.

If, now, these two lists are compared, it will be seen that while the values in both increase nearly equally for the lower values of K , they diverge when the values become higher, and, finally, for $K = 6$ (the largest value obtained for an element so far) the relative value of the energy storage is more than twice the value of the corresponding attraction.

Before proceeding further, it will be useful to plot the above results as curves with Columns 2 and 3 of Table II. as ordinates, and as abscissæ Atomic Weights or Numbers. Curves for both sets of properties do not essentially differ, but on the whole the relations appear a little more direct for Atomic Number than Weight, and therefore the curves below are worked out on this basis. Anyone, however, with the data can easily draw similar curves with abscissæ representing Atomic Weight.

Fig. 1.

Relation of Energy stored, and Attraction, to Atomic Number.



The intimate connexion between Atomic Weight and Number and the atomic ($K-1$) or dielectric equivalents of elements is manifest for the two groups Sulphur, Phosphorus, and Selenium, and secondly, Chlorine, Bromine, and Iodine, and also the corresponding relation with Atomic Attraction. These two sets of elements belong to well-defined and separate groups in the Periodic Table. Consequently, the connexion of the dielectric properties of these six elements with Atomic Weight, Number, and Position in the Periodic Table is well defined.

As regards the other four elements plotted, they each belong to separate groups in the Periodic Table, and data for further elements in these groups are so far wanting. The

evidence of the first six elements, however, permits a fair inference that the dielectric properties of these four elements also must probably be related in a similar way to Atomic Weight, Number, and Position in the Periodic Table. Further evidence that such is the case can be obtained by study of the optical properties of the dielectric elements on the above lines, as the optical data for a larger number of elements are known.

Further inferences can be drawn from study of this and other somewhat similar diagrams. Enough for the present purpose, however, has been said here in drawing attention to the fact that the electric properties of the elements are in the first place closely related to their Atomic Numbers and Weights, and in the second to their position in the Periodic Table. Their ordinary dielectric properties are, therefore, related to their chemical and physical properties in a very fundamental manner. The point is further made manifest that though the curves for energy stored and for attraction both show equal regularity, as the atomic weight or number gets higher, the relative amount of electric energy atomically stored in an electric field increases progressively as compared with the values of the corresponding attractions.

The curves also support Faraday's original view that the action of electric fields on dielectrics is directly on their atoms or molecules.

Note 1.—Experience shows that the dielectric constants or equivalents of the elements, when free from absorption, have very small temperature coefficients like the refractive index. In all the elements dealt with here, Maxwell's law is obeyed fairly closely, that $K=N^2$, the square of the refractive index.

Note 2.—The above procedure is very similar to that used for obtaining atomic or molecular refractivities, from $\frac{N^2-1}{N^2+2}$, this being the Lorentz formula. Optical workers always, however, write :

$$\frac{N^2-1}{N^2+2} \times \frac{AW}{D} = \text{Atomic Refractivity.}$$

The procedure above is rather different. Instead of making the correction in one operation, the molecular value of $K-1$, or N^2-1 is first found from $(K-1)\frac{AW}{D}$, and the figure thus obtained is afterwards inserted in the Boltzmann or Lorentz equation.

For the small values or variations of N usually discussed in optical work, there is little difference between the results given by the two formulæ, but over such ranges as those above the difference may be as much as 16 per cent. It is submitted that the method adopted above is physically correct, and should be used for optical wave-lengths also.

Note 3.—In the above tables it has been necessary to take the dielectric constant of liquid hydrogen from the square of the refractive index. The dielectric constant of hydrogen gas agrees almost absolutely with N^2 . For oxygen and nitrogen both the gaseous and liquid dielectric constants agree closely with N^2 . There are also other reasons which lead to the conclusion that the dielectric constant of liquid hydrogen of the density taken above is 121. The risk in assuming this value seems almost *nil*. Again, if it were incorrect the general conclusions arrived at would only be slightly affected.

It would appear that with modern methods of electric measurement and the means there are now of producing large quantities of liquid hydrogen, it should not be impossible to get the dielectric constant directly.

*Comparisons of the Relative Electric Values found with the
Relative Values of other Physical Properties.*

General Observations.

If dielectrics are taken at zero temperature (absolute), their molecules are not subject to the alternate attractions and repulsions of the electromagnetic waves of heat passing over them, and no heat is stored in the substance. Again, the molecules are in the closest proximity to each other, and any attractions between them are of the maximum strength.

Suppose these molecules, while at rest, are subjected to the action of heat waves which are also electromagnetic waves or pulses of gradually increasing intensity. They will be acted on by the waves and will also be alternately attracted and repelled as the waves pass over them. Thus they will be thrown into a state of vibration of gradually increasing amplitude. That is, the heat waves will introduce forces which, on the whole, oppose the natural attraction of the molecules for each other. As to this, Nernst, in his 'Theory of the Solid State,' says:—

“*Melting Point.*—Lindemann introduced the hypothesis that the melting point is determined by the fact that at this temperature the amplitude of the vibrations of the atoms round their positions of rest becomes commensurable with the atomic distances.”

If this is so, when the vibrations reach this amplitude the electric lines of force uniting the atoms or molecules can no longer be constantly directed to one set of neighbouring atoms, but they will equally be directed momentarily to others; consequently the force of cohesion, if this is electrical, will be largely nullified, and the tendency of the natural attractions to keep the substance in a definite formation will be overcome. Thus a considerable change of state will occur.

It seemed that, if there were substantial ground for this belief, some signs of connexion might be found between the relative absolute melting-points and the relative values either of the molecular energy stored in an electric field, or of the corresponding attractions, and comparison was made on the following lines.

Comparison of Electric Actions with Absolute Melting-Points.

Taking the absolute zero of temperature as basis, the relative values of the melting-points of the elements above this were found. Next, the melting-point of liquid hydrogen being definitely abnormal (a matter which will be referred to again later), that of liquid oxygen was taken as the standard and called 2, to agree with the relative values of both electrical actions. The relative values of the melting-point for the other elements were then divided by half the value for oxygen. The final set of proportional values thus found is given in Table III., column 4, where it can be compared with the relative values of the electrical energy reversibly stored (column 2), and, again, with the corresponding attractions (column 3).

TABLE III.

Relative Values of Different Physical Properties.

Elements.	Electric.		Thermal.	
	Energy stored.	Attractions.	Melting Points.	Boiling Points.
Hydrogen	1.0	1.0	0.5	0.5
Nitrogen	2.4	2.27	2.3	2.33
Oxygen	2.0	1.98	2.0	2.00
Carbon	5.2	4.5	—	—
Chlorine	7.7	6.1	5.4	6.0
Bromine	17.8	10.5*	8.4	8.4
Iodine	27.7	13.3	12.2	11.4
Phosphorus	16.2	10.0	10.0	9.0
Sulphur	16.2	10.1	12.2	17.9*
Selenium	32.2	14.3	15.6	24.0*

* See observations below.

The connexion between the relative melting-points and both electrical actions is evident, but is much more direct over the whole range for the attractions than for energy stored. In fact, the corresponding relative values of the attractions to the melting-points are so close in some cases that they approach coincidences. There is also reason to believe that if the fundamental electrical data were more accurately determined the correspondences might be still clearer.

It is hardly possible that there should be such a series of correspondences over such a range unless an intimate fundamental connexion underlay both physical actions.

The connexion predicated is, from the nature of all the actions, electric attraction. If this is accepted, it then seems to follow that the attraction of an outside electrical field for the molecules of a dielectric must actually be a fairly close proportional measure of the attractions of the molecules themselves for each other. This implication is further emphasized if, in addition to comparisons with melting-points, we next make them with the corresponding boiling-points.

Comparison with Absolute Boiling-Points.

Proceeding in the same way as with the melting-points, a table of the relative values of these was got out, using the absolute zero as a basis as before. The relative values of the boiling-points are given in Table III., column 5. With two exceptions, the coincidences are again practically as close as with the melting-points. As regards the differences, and one or two other points in the two tables, the following observations may be made.

The values for hydrogen come to about half the values for the corresponding dielectric equivalents, and in the boiling-point table the values for sulphur and selenium are about 50 per cent. too high. The first of these differences may be connected with the change in the specific heat of hydrogen between the liquid and gaseous state. In the second case, Ramsay points out in his 'Chemistry' that, at the temperature necessary to bring sulphur and selenium to the boiling-point, there is preliminary molecular dissociation in addition to simple change of state, thus raising the boiling-point. It is proposed to defer further discussion of these and some other matters until later.

Again, recent experimental work on bromine leads to the view that the accepted dielectric constant is rather high. Further experiments are in progress to test this, for which

Professor H. B. Baker has kindly supplied his highly dried bromine. It is hoped to report the results later.

As regards the importance of the melting and boiling points in arriving at a more complete knowledge of the constitution of matter, two further passages from Nernst's work already mentioned may be quoted.

"An especially simple significance attaches to the work which must be expended to break up a solid body into its constituent molecules, and to separate these molecules to definite distances from one another. *The latter occurs when a solid body is sublimed.*

"For crystalline substances—and we shall always (unless otherwise stated) picture to ourselves a solid body as a crystal, since the amorphous state is known to be a continuous transition of the liquid state of aggregation—the melting point is a specially characteristic magnitude."

Relation of Relative Molecular Electric Actions to Heat of Vaporization.

The question next arose whether the correspondences so far found would still persist for the relative heats of vaporization. The data I have been able to find only extend to six elements, and one of these, viz. iodine, has to be melted at a considerably higher temperature than the others before being vaporized. The heat necessary to change iodine from a solid to a liquid is, however, available and has been added in this case. The conditions generally do not allow of comparison to a close percentage of accuracy, but the relative values come out as follows :—

TABLE IV.

Relative Molecular Amounts of Heat Absorbed in Change from Liquid or Solid State to Vapour.

Elements.	Relative Values of Vaporization.	Molecular Attractions.
1.	2.	3.
Hydrogen.....	·5	1·0
Nitrogen.....	1·8	2·3
Oxygen	2·0	2·0
Chlorine	5·4	6·1
Bromine	9·5	10·5
Iodine	12·0	13·3

In this case, though the agreement is ostensibly with the corresponding relative attractions, relative heats of

vaporization should be more naturally comparable with relative amounts of energy reversibly stored or $(K_m - 1)$. As regards this, it will be seen from Table II. that the relative values for energy stored, or $(K_m - 1)$, and for the attractions have practically the same ratios for the three elementary gases in liquid form. Investigation shows that they have also the same ratios in the gaseous form. As regards liquid chlorine and the other elements where differences begin to appear, there is further evidence which seems to lead to the view that the relative values of the energy reversibly stored $(K - 1)$ and of the corresponding attractions preserve a fairly constant ratio from element to element when these elements are in the state of gas or vapour; the relative increases in energy stored arise in the liquid and solid states or as aggregation increases. This point will be referred to again later.

Further Considerations.

Trouton's rule states that, with certain remarkable exceptions (viz. helium and hydrogen),

$$\frac{\text{Heat of vaporization}}{\text{Boiling temp. (abs.)}} = \text{constant.}$$

Now we have seen above that the relative values of both these quantities agree with the relative values of the corresponding electric attractions for different elements. We can therefore apparently re-write Trouton's rule and say:

$$\frac{\text{Electric attraction overcome in vaporization}}{\text{Electric attraction overcome at boiling-point}} = \text{constant,}$$

remembering that the attraction in vaporization is also proportional to energy stored.

Again, it is pointed out in such works as Nernst's 'Theoretical Chemistry' that if the absolute melting-points of substances are taken as 2 in each case, the absolute boiling-points have approximately relative values of 3, and the critical temperatures of 4, and the connexion between them and the heat of vaporization is given by Trouton's rule. Consequently, the electric attractions, as shown above, are intimately connected with, and must be more or less proportional to, the values of all these properties, including the critical temperature in each of the elements we are dealing with.

But the relation of the boiling-points to the values of

osmotic pressure is further well recognized, and osmotic pressures can be found by the lowering of the freezing-point or the raising of the boiling-point in the case of Solutes. Consequently it seems to follow that there are also intimate relations between the electric attractions and osmotic pressure in addition to the connexions shown above.

It is impossible here to go into all these actions in detail, but as it is already recognized that all this group of fundamental interactions between heat and matter are interconnected, if what has been said above is in principle correct, the basis of the connexion is evidently the electric attraction of the molecules of different substances for each other, and this attraction can be found in the case of dielectrics by the method worked out by Boltzmann in 1873, when extended as above.

The above results further seem to show that the atomic or molecular electric attractions involved are of the usual character and obey the ordinary electric laws.

Relations of Energy Reversibly Stored in Electric Actions to the Energy Stored in Heat Actions.

Though in dielectrics the primary connexion has been shown to be with electric attraction and not with energy stored, nevertheless electric attraction and the electric energy stored in dielectrics in electric fields are closely related, since we can measure them both, and by Boltzmann's formula can derive one from the other. The question then arises why the relation is so direct for the attraction while the energy stored under the same conditions shows increasing differences from the corresponding attractions as we progress from liquids at very low temperatures to liquids at ordinary temperatures, and still more markedly to solids.

The answer, apparently, is that when we measure the capacity of a dielectric we are measuring the energy reversibly stored in it in several different ways:—

- (1) Between the boundaries of the field.
- (2) In polarizing internally the individual atoms and molecules or changing them into doublets, and thus altering their attraction for each other also.
- (3) In displacing the atoms or molecules bodily and setting them into vibration.
- (4) In effecting smaller concurrent changes.

The reason why hitherto so little correspondence has been found between the values of the dielectric constant of substances and other physical actions is evidently because we must know something of the relative values of the energy involved in the above different actions separately before clear and quantitative connexions can be established.

If we turn to the phenomena of heat, it has for a long time been accepted that, when a substance is put in an alternating field of the frequency of heat waves, the energy impressed, in the case of solids, is stored in different ways, of which two account for the greater part in more or less equal proportions (see Nernst's 'Physical Chemistry,' 1913, p. 260).

It seems probable that as heat energy is stored in a dielectric in these different ways, the same, or nearly so, may be the case when dielectrics are placed in ordinary electric fields, and that more energy may be stored for a given stress in some cases than others.

Now if the lists of the relative values of the attractions and energy stored (Table II.) are examined, it will be found that there are differences between the relative values of the attractions and energy stored in the case of the solids of the order of those suggested by thermodynamic theory, the differences falling off from solid to liquid and liquid to gas.

I do not put forward this as more than suggestive at the present stage, but further experiments are practicable which would throw a much clearer light on this part of the subject.

Relations of Electrical to Mechanical Attraction.

The above comparisons have been made between the actions of ordinary electric fields on matter and those of heat. It is possible, however, to make comparisons of a more direct nature, in which the electric attraction is compared directly with mechanical forces or pulls.

Relations with Surface Tension.

The cohesion of different kinds of elementary matter must be allied more or less directly with the corresponding surface tension. Unfortunately the surface tensions of only a few of the elements we are dealing with are available, and have necessarily been obtained under somewhat different conditions; but the relative molecular values show an unmistakable connexion with the corresponding values for the electric attractions.

The data in the Table below were kindly corrected by Mr. Hatschek. He also raised the point of the basis on which calculations should be made. They have been made on the assumption that the active atoms are a single surface layer. The numbers of atoms in a given length will therefore be inversely proportional to their diameters. These have been calculated from the atomic volumes given above.

The columns in the table below show:—

1. Observed superficial tension in dynes per cm. The letters indicate the temperatures. B, near boiling point, F, fusion point; in two cases the temperatures are given.
2. Relative Superficial Tensions taking Oxygen (2) as basis.
3. Relative atomic diameters taking that of Oxygen as unity.
4. Relative atomic tension (Col. 2) \times (Col. 3).
5. Corresponding relative atomic electric attractions.

TABLE V.

Element.	Surface Tension Actual.	Surface Tension Relative.	Atomic Diameter Relative.	Surface Tensions Atomic.	Electr. Attrac. Atomic.
Oxygen	13.0 B	2.0	1.00	2.0	2.0
Chlorine.....	33 -72°	5.2	1.23	6.4	6.2
Bromine.....	62 +21°	9.4	1.25	11.7	10.0
Phosphorus	41.0 F	6.2	1.1	6.8	10.0
Sulphur.....	42.0 F	6.2	1.2	7.4	10.0
Selenium	70.0 F	10.7	1.15	12.3	14.25

The results can only be a first approximation, but they seem definite enough to show an intimate relation with electric attraction which would probably be closer could proper corrections be applied. The greatest differences are with phosphorus and sulphur which behave rather indefinitely about the melting point.

These results connect the electric properties directly with the forces of cohesion. It must be remembered, however, that the actual forces in cohesion as found in solids in the mass are also dependent on molecular aggregation and crystallization. The forces of cohesion between a mass of crystals may differ widely from the forces within a single crystal.

Surface Tension has already been connected with latent heat : see 'Surface Tension and Surface Energy,' Willows and Hatschek, p. 11. Consequently there is a connexion between latent heat and the electrical properties also.

Comparison with Capillarity.

Here again we can compare the electrical pull with the mechanical, but with the interesting difference that the atoms are separate and much more in the same state as in the gaseous condition.

When liquids are brought into contact with the surface of solids, attraction usually takes place.

Early work showed that small percentages of salts in the water usually increased this attraction in different degrees. The salt in such solutions is ionized and exists in the form of oppositely charged ions, only one kind of which will be attracted by the glass, namely, that having the opposite charge to the glass.

By a large number of comparative experiments on salts of varying composition, Schiff (see Smiles's 'Chemical Constitution and Some Physical Properties,' p. 34) arrived at an estimate of the relative attraction values of the separate ions in the case of six of the elements we are dealing with. These comparative values are given in Table VI. in terms of hydrogen. They agree substantially with the relative values of the dielectric attractions. There are similar relations, though not numerically so close, with viscosity.

TABLE VI.

Elements.	Capillarity.	
	Relative Tensions.	Relative Molecular Attractions.
Hydrogen	1	1
Nitrogen	2—3	2.4
Oxygen	2—3	2.0
Chlorine	6—7	5.9
Bromine	11—13	10.5
Iodine	19*	13.3

* With iodine there is apparently dissociation.

There are certain margins in these correspondences, due no doubt to the difficulty of exact experiment, and also to the fact that some dissociation must have taken place in one or two cases ; for instance, in the case of iodine.

The correspondences, however, are sufficiently close to predicate an intimate connexion between the attraction of the separate ions of an element for the glass used as a standard of attraction and the corresponding attractions of an electric field for the same ions aggregated together in an ordinary state. The results show that the character of this natural attractive force is apparently only fractionally altered when the molecules are aggregated, as compared with what it is when they exist separately in a solution.

Finally, it is to be observed that, while water with different salt solutes has been used as above for finding variations in capillary attractions, the solutions are essentially electrolytic, and similar to those used by Gladstone and Dale for obtaining specific refractivities.

Maxwell's Relation and the Relations of Electric Energy Stored and the Corresponding Attractions to Optical Phenomena.

In addition to the correspondences found above, there are similar, and in some cases even closer, relations with the so-called "optical properties."

In all that has been said so far, reference to the optical relations has been avoided in order to establish the results from the purely electrical standpoint.

Maxwell's relation that K should equal N^2 is, however, verified—at least the two quantities are closely of the same order—for all the elements dealt with here, and there is evidence that the same is also most probably the case for the rest of the nineteen dielectric elements, or at any rate for sixteen of them.

Consequently, with fair approximation, we have for all the above elements :

$$K_m - 1 = N_m^2 - 1 \quad \text{and} \quad \frac{K_m - 1}{K_m + 2} = \frac{N_m^2 - 1}{N_m^2 + 2},$$

the latter being the Lorentz formula. As used in optics, the two formulæ have had a theoretical basis, but as for long waves they are associated directly with energy stored and with attraction respectively, it seems a fair inference that they must be similarly associated with the similar actions occurring at the frequencies of light and heat.

Since in both cases we start with fair coincidence, if two lists of relative values for $N_m^2 - 1$ and $\frac{N_m^2 - 1}{N_m^2 + 2}$ are made on the same lines as above, the figures obtained

for all the elements will correspond, except for fractional differences, with those already found above on a purely electrical basis.

Conclusion.

In the case of surface tension and capillarity, a static or gravitational pull is balanced against the steady electric attraction of the molecules for each other or for a standard. In the melting and boiling points, the disruptive or shaking action of the electric waves is balanced against the steady natural electric attraction between the molecules. Thirdly, in vaporization the connexion seems to be with the energy stored, which is also proportionate to the attraction. Finally, heat and light waves so overlap in frequency that what is true for the one must almost certainly follow (speaking generally) for the other.

The difference between the effects of long electric waves and short in dielectrics seems chiefly to lie in the fact that with long waves we have a single potential slope throughout the dielectric, while with light and heat waves there are nearly always a number of complete waves in its thickness. Consequently, some of the molecular condensers subjected to light and heat waves are receiving a charge at the same time that others are discharging. This causes important differences, but rather of detail than of principle, and chiefly in the initial application and dying down of the field.

Thus, as outlined above, the electric attraction and the phenomena of capacity in dielectrics can be brought into line, speaking generally, with work which has been done optically or at light frequencies, and both are brought into close relation with the phenomena of heat, surface tension (which is closely allied with cohesion), and capillarity.

Space here only permits of allusion to the further connexions which exist between the electrical properties of these elements as defined above and their atomic weight or number, position in the Periodic Table, and chemical action. It is hoped to discuss these later.

The substances dealt with above include the two elements (hydrogen and oxygen) from which water is formed, and also the four elements (hydrogen, oxygen, nitrogen, and carbon) which are the basis of all organic compounds. If chlorine, sulphur, and phosphorus are added to these we have also the main constituents (apart from calcium, silicon, and sodium) of all animal and vegetable life. They also include the elements composing most of the dielectrics used in science and engineering.

The importance of obtaining the electrical properties of these dielectric elements exactly, and of connecting them with other physical properties, is thus obvious. Again, these elements form a number of compounds between themselves, the electrical properties of which can also be measured, and thus a sound basis can be established for finding the electrical effects of chemical combination.

Having got as far as has been shown above in connecting the ordinary electrical phenomena in these elements with the effects of heat, it seems almost certain that a further close connexion must exist between the electric actions and the specific heats of these elements.

I have to thank Dr. Thornton, Mr. R. Appleyard, Mr. E. E. Brooks and others for kind help and criticism in putting the above work into shape.

XCV. *A Simple Formal Solution of the General Equations of Elastic Stress.* By R. F. GWYTHER, M.A.*

THE solution given here is derived from those given in a previous paper on "An Analytical Discrimination of Elastic Stresses in an Isotropic Body" †.

1. The solutions indicated in that paper, in the case where no bodily forces are acting, may be briefly re-stated as follows:—

$$\begin{aligned}
 P = & - \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \bar{\theta} - \frac{\partial^2 \theta_3}{\partial y^2} - \frac{\partial^2 \theta_2}{\partial z^2} \\
 & - \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \bar{\psi} + 2 \frac{\partial^2 \psi_1}{\partial y \partial z}, \\
 \dots = & \dots \dots \dots \\
 S = & \frac{\partial^2 \bar{\theta}}{\partial y \partial z} + \frac{\partial^2 \theta_1}{\partial y \partial z} \\
 & + \frac{\partial^2 \bar{\psi}}{\partial y \partial z} + \frac{\partial^2 \psi_1}{\partial z^2} - \frac{\partial^2 \psi_2}{\partial x \partial y} - \frac{\partial^2 \psi_3}{\partial x \partial z}, \\
 \dots = & \dots \dots \dots \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)
 \end{aligned}$$

* Communicated by the Author.

† Phil. Mag. July 1922, p. 274.

where

$$(m+n)\nabla^2\bar{\theta}=2m\left(\frac{\partial^2\theta_1}{\partial x^2}+\frac{\partial^2\theta_2}{\partial y^2}+\frac{\partial^2\theta_3}{\partial z^2}\right),$$

and

$$(m+n)\nabla^2\bar{\psi}=4m\left(\frac{\partial^2\psi_1}{\partial y\partial z}+\frac{\partial^2\psi_2}{\partial x\partial z}+\frac{\partial^2\psi_3}{\partial x\partial y}\right), \quad (2)$$

and where $\theta_1, \theta_2, \theta_3, \psi_1, \psi_2, \psi_3$ are Spherical Harmonic Functions.

The terms in the upper lines throughout, and in the lower lines throughout, form independent and general values of the elements of elastic stress.

If we write the components of bodily force per unit of mass in the form

$$\begin{aligned} -\frac{\partial V}{\partial x}-\frac{\partial W_3}{\partial y}-\frac{\partial W_2}{\partial z}, & \quad -\frac{\partial V}{\partial y}-\frac{\partial W_1}{\partial z}-\frac{\partial W_3}{\partial x}, \\ -\frac{\partial V}{\partial z}-\frac{\partial W_2}{\partial x}-\frac{\partial W_1}{\partial y}, & \end{aligned}$$

we must then add ρV to the value of each P, Q, and R, and $\rho W_1, \rho W_2, \rho W_3$ to the values of S, T, U respectively given in (1) in order to satisfy the stress equations.

Since the equations are linear, we may consider each case separately, and collect the results.

Taking the terms in V, we may employ the solutions in the upper lines or in the lower lines of (1) indiscriminately, and write

$$\begin{aligned} P &= \rho V - \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \phi, \\ Q &= \rho V - \left(\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial x^2} \right) \phi, \\ R &= \rho V - \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \phi, \\ S &= \frac{\partial^2 \phi}{\partial y \partial z}, \quad T = \frac{\partial^2 \phi}{\partial x \partial z}, \quad U = \frac{\partial^2 \phi}{\partial x \partial y}, \quad \dots \quad (3) \end{aligned}$$

where the components of the displacement are given by

$$2nu = \frac{\partial \phi}{\partial x}, \quad 2nv = \frac{\partial \phi}{\partial y}, \quad 2nw = \frac{\partial \phi}{\partial z}, \quad \dots \quad (4)$$

and the only condition requisite that the stress may be elastic is that

$$(m+n)\nabla^2\phi=2n\rho V. \quad \dots \quad (5)$$

If, for example,

$$V = \int \frac{dM_1}{r_1},$$

then
$$\phi = \frac{n\rho}{m+n} \int r_1 dM_1.$$

The terms arising from V are now considered as completed.

Turning then to the terms in W , we shall find the solutions given in the lower lines the more convenient, and will write :

$$\begin{aligned} P &= - \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + 2 \frac{\partial^2 \psi_1}{\partial y \partial z}, \\ &\dots = \dots \dots \\ S &= W_1 + \frac{\partial^2 \bar{\psi}}{\partial y \partial z} + \frac{\partial^2 \psi}{\partial x^2} - \frac{\partial^2 \psi_2}{\partial x \partial y} - \frac{\partial^2 \psi_3}{\partial x \partial z}, \\ &\dots = \dots \dots, \end{aligned} \quad (6)$$

where

$$2nu = \frac{\partial \bar{\psi}}{\partial x} - 2 \frac{\partial \psi_3}{\partial y} - 2 \frac{\partial \psi_2}{\partial z}, \text{ etc.} \quad (7)$$

The conditions requisite for elastic stresses are

$$(1) \text{ that } S = n \left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \text{ etc.,}$$

from which we find in turn

$$W_1 + \nabla^2 \psi_1 = 0, \quad W_2 + \nabla^2 \psi_2 = 0, \quad W_3 + \nabla^2 \psi_3 = 0; \quad (8)$$

$$(2) \text{ that } P - Q = 2n \left(\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} \right), \text{ etc.,}$$

which are satisfied identically,

$$\text{and } (3) \text{ that } P + Q + R = (3m - n) \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right),$$

whence

$$(m+n) \nabla^2 \bar{\psi} = 4m \left(\frac{\partial^2 \psi_1}{\partial y \partial z} + \frac{\partial^2 \psi_2}{\partial x \partial z} + \frac{\partial^2 \psi_3}{\partial x \partial y} \right). \quad (9)$$

2. The simplification which I am about to introduce arises from the substitution of a single term to stand for each of the expressions

$$\frac{\partial \psi_3}{\partial y} + \frac{\partial \psi_2}{\partial z}, \quad \frac{\partial \psi_1}{\partial z} + \frac{\partial \psi_3}{\partial x}, \quad \frac{\partial \psi_2}{\partial x} + \frac{\partial \psi_1}{\partial y}$$

in the values of $2nu$, etc., given in (7). However, guided

by experience gained in obtaining the foregoing results, I shall also alter the method of investigation by reversing the order of the steps, and shall secure that the elements of stress satisfy the conditions for being elements of elastic stress first, and that the stress equations are satisfied as the final step.

Accordingly I shall write

$$2nu = \frac{\partial \bar{\phi}}{\partial x} - 2\phi_1, \quad 2nv = \frac{\partial \bar{\phi}}{\partial y} - 2\phi_2, \quad 2nw = \frac{\partial \bar{\phi}}{\partial z} - 2\phi_3, \quad (10)$$

and

$$\begin{aligned} P &= -\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\bar{\phi} - \frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y} + \frac{\partial \phi_3}{\partial z}, \\ Q &= -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2}\right)\bar{\phi} + \frac{\partial \phi_1}{\partial x} - \frac{\partial \phi_2}{\partial y} + \frac{\partial \phi_3}{\partial z}, \\ R &= -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\bar{\phi} + \frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y} - \frac{\partial \phi_3}{\partial z}, \\ S &= \frac{\partial^2 \bar{\phi}}{\partial y \partial z} - \frac{\partial \phi_3}{\partial y} - \frac{\partial \phi_2}{\partial z}, \\ T &= \frac{\partial^2 \bar{\phi}}{\partial x \partial z} - \frac{\partial \phi_1}{\partial z} - \frac{\partial \phi_3}{\partial x}, \\ U &= \frac{\partial^2 \bar{\phi}}{\partial x \partial y} - \frac{\partial \phi_2}{\partial x} - \frac{\partial \phi_1}{\partial y} \dots \dots \dots (11) \end{aligned}$$

In this case the conditions that

$$\begin{aligned} S &= n\left(\frac{\partial v}{\partial y} + \frac{\partial v}{\partial z}\right), \quad T = n\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right), \quad S = n\left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right), \\ P - Q &= 2n\left(\frac{\partial u}{\partial x} - \frac{\partial v}{\partial y}\right), \quad P - R = 2n\left(\frac{\partial u}{\partial x} - \frac{\partial w}{\partial z}\right), \end{aligned}$$

are all satisfied identically, and the condition that

$$P + Q + R = (3m - n)\left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right)$$

requires that

$$(m + n)\nabla^2 \bar{\phi} = 2m\left(\frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y} + \frac{\partial \phi_3}{\partial z}\right) \dots \dots (12)$$

Substituting in the stress equation, we shall find, if X, Y, Z are the components of bodily force per unit of mass in excess of the terms already considered, viz.

$$\begin{aligned} -\frac{\partial V}{\partial x}, \quad -\frac{\partial V}{\partial y}, \quad -\frac{\partial V}{\partial z}, \\ \nabla^2 \phi_1 = \rho X, \quad \nabla^2 \phi_2 = \rho Y, \quad \nabla^2 \phi_3 = \rho Z. \dots (13) \end{aligned}$$

The equations (11) with the conditions (12) and (13) give the simple solution I have to offer, and the components of the displacement are given by (10). The basis of the simplification consists in the reduction of the degree of many of the differential coefficients as compared with the solutions as given by (1). Since the terms thus simplified do not enter the solutions embodied in (3) and (5), there is no simplification in that case.

In the case of a whirling body considered on page 283 of the paper previously referred to, the reversed effective forces have components, beyond those which may be included in

$$-\rho \frac{\partial V}{\partial x}, \quad -\rho \frac{\partial V}{\partial y}, \quad -\rho \frac{\partial V}{\partial z},$$

dealing with angular velocities, viz.

$$\rho(y\dot{\omega}_z - z\dot{\omega}_y), \quad \rho(z\dot{\omega}_x - x\dot{\omega}_z), \quad \rho(x\dot{\omega}_y - y\dot{\omega}_x),$$

dealing with the rates of change of the angular velocities. These will replace $\rho X, \rho Y, \rho Z$ in (13), so that

$$\nabla^2 \phi_1 = \rho(v\dot{\omega}_z - z\dot{\omega}_y), \text{ etc.}$$

Since the solutions arising from bodily forces are Particular solutions, we may write

$$\phi_1 = \frac{1}{2} \rho x^2 (y\dot{\omega}_z - z\dot{\omega}_y), \text{ etc.,}$$

and so find

$$\frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y} + \frac{\partial \phi_3}{\partial z} = 0,$$

and we may treat ϕ as null for the reason given above.

Hence from (11), in this case*,

$$P = -2\rho x(y\dot{\omega}_z - z\dot{\omega}_y), \text{ etc.,}$$

$$S = -\frac{1}{2} \rho \dot{\omega}_x (y^2 - z^2), \text{ etc.,}$$

$$\text{with} \quad 2nu = -\rho x^2 (y\dot{\omega}_z - z\dot{\omega}_y), \text{ etc.,}$$

and the results are independent of the ratio m/n , while they satisfy the analytical conditions for elastic stresses.

When in (13) X, Y, Z are made null, we have the conditions that ϕ_1, ϕ_2, ϕ_3 shall be Spherical Harmonic Functions, and, with these additional conditions, equations (11) and (12) give the elastic stresses which are Complementary solutions when bodily forces are acting, and are the complete solutions when the body is subject to tractions only.

* This replaces an erroneous paragraph (the fourth) on page 283.

The full form of solution under general bodily forces will be collected from (3) and (11) with their respective conditions and with the Complementary solutions consequent on treating the bodily forces as null.

3. As an illustration of these Complementary solutions we may write

$$\phi_1 = \int \frac{dM_1}{r_1}, \text{ etc.,}$$

where $r_1^2 = (x-x_1)^2 + (y-y_1)^2 + (z-z_1)^2,$

and $dM_1 = \rho_1 dx_1 dy_1 dz_1$

with the condition that r_1 shall never be zero, with corresponding expressions for ϕ_2 and ϕ_3 .

Then

$$\bar{\phi} = \frac{m}{m+n} \left\{ \int \frac{x-x_1}{r_1} dM_1 + \int \frac{y-y_2}{r_2} dM_2 + \int \frac{z-z_3}{r_3} dM_3 \right\}.$$

Retaining only the terms with subscript 1, we find a system of elastic stresses

$$P = \frac{3m}{m+n} \int \frac{(x-x_1)^3}{r_1^5} dM_1 + \frac{n}{m+n} \int \frac{x-x_1}{r_1^3} dM_1,$$

$$Q = \frac{3m}{m+n} \int \frac{(x-x_1)(y-y_1)^2}{r_1^5} dM_1 - \frac{n}{m+n} \int \frac{x-x_1}{r_1^3} dM_1,$$

$$R = \frac{3m}{m+n} \int \frac{(x-x_1)(z-z_1)^2}{r_1^5} dM_1 - \frac{n}{m+n} \int \frac{x-x_1}{r_1^3} dM_1,$$

$$S = \frac{3m}{m+n} \int \frac{(x-x_1)(y-y_1)(z-z_1)}{r_1^5} dM_1,$$

$$T = \frac{3m}{m+n} \int \frac{(x-x_1)^2(z-z_1)}{r_1^5} dM_1 + \frac{n}{m+n} \int \frac{z-z_1}{r_1^3} dM_1,$$

$$U = \frac{3m}{m+n} \int \frac{(x-x_1)^2(y-y_1)}{r_1^5} dM_1 + \frac{n}{m+n} \int \frac{y-y_1}{r_1^3} dM_1. \quad (14)$$

4. Extension to general orthogonal coordinate systems.

It is clear that in these systems we may form expressions for the elements of stress and coordinates of displacement cognate to those for the cartesian system which are contained in equations (11), (12), and (13) and that a measure of simplification will result of the same general character as in the cartesian system though naturally less in degree.

Thus we should write

$$P = -h_2^2 \frac{\partial^2 \phi}{\partial \eta^2} - h_3^2 \frac{\partial^2 \phi}{\partial \xi^2} + h_1^2 \left(\frac{1}{h_2} \frac{\partial h_2}{\partial \xi} + \frac{1}{h_3} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial \phi}{\partial \xi} \\ - h_2 \left(\frac{\partial h_2}{\partial \eta} - \frac{h_2}{h_3} \frac{\partial h_3}{\partial \eta} \right) \frac{\partial \phi}{\partial \eta} - h_3 \left(\frac{\partial h_3}{\partial \xi} - \frac{h_3}{h_2} \frac{\partial h_2}{\partial \xi} \right) \frac{\partial \phi}{\partial \xi} - e' + f' + g', \\ \dots = \dots$$

$$S = h_2 h_3 \frac{\partial^2 \phi}{\partial \eta \partial \xi} + h_3 \frac{\partial h_2}{\partial \xi} \frac{\partial \phi}{\partial \eta} + h_2 \frac{\partial h_3}{\partial \eta} \frac{\partial \phi}{\partial \xi} - a', \quad \dots \quad (15) \\ \dots = \dots$$

and

$$2nu = h_1 \frac{\partial \phi}{\partial \xi} - 2\phi_1, \quad 2nv = h_2 \frac{\partial \phi}{\partial \eta} - 2\phi_2, \quad 2nw = h_3 \frac{\partial \phi}{\partial \xi} - 2\phi_3, \quad (16)$$

where $\{e', f', g', a', b', c'\}$ are related to ϕ_1, ϕ_2, ϕ_3 as, in the usual notation of the subject, $\{e, f, g, a, b, c\}$ are related to u, v, w . The terms in ϕ in the expressions for the elements of stress are derived from the solutions of the Stress Equations as given by me *, when $\theta_1, \theta_2, \theta_3$ are each replaced by ϕ .

By making use of the expressions for the elements of strain, we may verify that

$$S = na, \quad T = nb, \quad U = nc,$$

$$P - Q = 2n(e - f), \quad P - R = 2n(e - g) \text{ are satisfied.}$$

The remaining condition to secure the elastic nature of the stress, namely

$$P + Q + R = (3m - n)(e + f + g),$$

becomes on substitution

$$(m + n) \nabla^2 \phi = 2m(e' + f' + g') \\ = 2mh_1 h_2 h_3 \left\{ \frac{\partial}{\partial \xi} \left(\frac{\phi_1}{h_2 h_3} \right) + \frac{\partial}{\partial \eta} \left(\frac{\phi_2}{h_3 h_1} \right) + \frac{\partial}{\partial \xi} \left(\frac{\phi_3}{h_1 h_2} \right) \right\}. \quad (17)$$

If we now substitute for the elements of stress in the Stress Equations, the terms in ϕ will disappear, since they are known to satisfy identically the equations under tractions only, and the remaining terms contain ϕ_1, ϕ_2, ϕ_3 only.

The final quantities which are to be equated to $\rho X, \rho Y, \rho Z$,

* Phil. Mag. Sept. 1923, p. 482.

or to zero, as the case may be, become

$$\begin{aligned} \nabla^2 \phi_1 - \left\{ \frac{h_1^2}{h_2^2} \left(\frac{\partial h_2}{\partial \xi} \right)^2 + \frac{h_2^2}{h_1^2} \left(\frac{\partial h_1}{\partial \eta} \right)^2 + \frac{h_1^2}{h_3^2} \left(\frac{\partial h_3}{\partial \xi} \right)^2 + \frac{h_3^2}{h_1^2} \left(\frac{\partial h_1}{\partial \zeta} \right)^2 \right\} \phi_1 \\ - 2h_2 \frac{\partial h_1}{\partial \eta} \frac{\partial \phi_2}{\partial \xi} + 2h_1 \frac{\partial h_2}{\partial \xi} \frac{\partial \phi_2}{\partial \eta} - 2h_3 \frac{\partial h_1}{\partial \zeta} \frac{\partial \phi_3}{\partial \xi} + 2h_1 \frac{\partial h_3}{\partial \xi} \frac{\partial \phi_3}{\partial \zeta} \\ + \left\{ h_1 \frac{\partial^2 h_2}{\partial \xi \partial \eta} - h_2 \frac{\partial^2 h_1}{\partial \xi \partial \eta} + \frac{h_2}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_1}{\partial \eta} - \frac{h_1}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_2}{\partial \eta} \right. \\ \left. - \frac{h_1 h_2}{h_3^2} \frac{\partial h_3}{\partial \xi} \frac{\partial h_3}{\partial \eta} + \frac{h_2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial h_1}{\partial \eta} - \frac{h_1}{h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \eta} \right\} \phi_2, \\ + \left\{ h_1 \frac{\partial^2 h_3}{\partial \xi \partial \zeta} - h_3 \frac{\partial^2 h_1}{\partial \xi \partial \zeta} + \frac{h_3}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_1}{\partial \zeta} - \frac{h_1 h_3}{h_2^2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_2}{\partial \zeta} \right. \\ \left. - \frac{h_1}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial h_3}{\partial \zeta} + \frac{h_3}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_1}{\partial \zeta} - \frac{h_1}{h_2} \frac{\partial h_3}{\partial \xi} \frac{\partial h_2}{\partial \zeta} \right\} \phi_3, \quad (18) \end{aligned}$$

with two homologous expressions.

In spite of their length, these expressions constitute a very real simplification.

XCVI. *Convective Cooling in Liquids—Some Thermal Conductivity Data.* By A. H. DAVIS, M.Sc. (From the National Physical Laboratory*.)

THE author has recently given data† for the cooling of horizontal wires immersed in various liquids, and has correlated them, on the basis of hydrodynamical considerations, with the physical properties of the liquids concerned. In the work it was taken for granted that the thermal conductivities of the liquids were not markedly dependent upon temperature. However, C. W. Rice‡, apparently by analysing results for these liquids on the basis of a modification of Langmuir's film theory of convection, has deduced § positive temperature coefficients equivalent to about 1 per cent. increase in conductivity per degree temperature rise.

* Communicated by the Director.

† Phil. Mag. xliv. p. 920 (1922).

‡ Phys. Rev. xxi. p. 474, 1923 (Abstract).

§ With regard to the basis of Rice's calculations, it is difficult to see why his equation for film thickness contains the acceleration (g) due to gravity, while it omits the volume coefficient of expansion (α) of the fluid and the temperature excess of the body. For presumably it is through the vigour of the convection (gravity) currents set up that ' g ' affects the film thickness; and ' α ' is as important as ' g ' in determining these.

Such effects are rather large and are of opposite sign to those the present author had reason to expect. It was desirable, therefore, to carry out direct determinations of thermal conductivity at various temperatures, to supplement the information already given concerning the liquids in question.

Fortunately, apparatus which had been used in the convection experiments was readily adaptable to comparisons of thermal conductivity by the Goldschmidt * method, and a test was therefore carried out.

Apparatus.

The method consisted in stretching a fine platinum wire along the axis of a narrow horizontal silver tube full of the test liquid, and measuring the electric current necessary to maintain a measured temperature difference between the wire and the walls of the tube. A relative value of the thermal conductivity was thus obtained.

In the actual apparatus the silver tube, 2 mm. diameter and 12.7 cm. long, was fitted tightly into a massive copper cylinder of 5 cm. diameter, so that the temperature was uniform throughout its length. The axial wire was 1 mil (0.002 cm.) in diameter. A shorter length of the same wire, passing through another silver tube in the block, was used for the automatic compensation of any end-effects. The whole apparatus was completely immersed in a vessel full of the liquid to be examined, which thus filled the capillary tube. The vessel itself was immersed in a carefully designed water-bath kept well-stirred at constant temperature.

Using a Wheatstone Bridge arrangement for the necessary resistance measurements, determinations were made of the heat dissipation associated with various small temperature excesses of the wire, ranging from 1° or 2° C. to 10° or 20° C. For moderate heating the results were almost completely independent of the temperature excess, whence it may be inferred that convection currents were inappreciable. The conductivity given later is the value to which results tended as the temperature excess was reduced.

Results.

For each liquid, experiments were carried out at two or three temperatures in the range 15° to 80° C. Provided the apparatus was not interfered with mechanically, values for the various temperatures were found to repeat accurately,

* *Phys. Zeits.* xii. p. 417 (1911).

deviations from the mean curve being generally less than 1 per cent. The relative values of the thermal conductivities of different liquids, however, were not reliable to better than ± 5 per cent., since the constant of the instrument changed within these limits when the apparatus was emptied, cleaned, and refilled.

Taking as standard the value given by Goldschmidt for toluol at air temperatures ($10^4 k = 3.42$) the mean results obtained have been summarized in Table I.

It appears that the thermal conductivity does not depend markedly upon the temperature of the liquid, and contrary to the calculations already referred to, the effect is generally a slight decrease as the temperature is raised.

I desire to thank Dr. G. W. C. Kaye for continuing the facilities afforded for the convection work. Mr. R. R. Strand assisted with the experimental arrangements and observations.

TABLE I.

Liquid.	Temperature (t).	Thermal Conductivity (cals. per cm. per °C.) (k).	Temperature coefficient †. (α).
Toluol	19° C.	3.4×10^{-4}	} -0.002
	69	3.1	
Carbon tetra- chloride ...	23	2.8	} -0.003
	68	2.4	
Olive oil * ...	19	4.0	} -0.000 ₈
	71	3.85	
Aniline	15	4.4	} -0.000 ₃
	73	4.35	

* With olive oil progressive discoloration was noticed as time went on, and the measured values of the thermal conductivity increased from day to day, presumably owing to contamination with copper.

† $k_t = k_0 (1 + \alpha t)$.

Note added February 1924.

Since this paper was written a more recent contribution by Rice (Am. I.E.E., J. xlii. p. 1288, Dec. 1923) has been published. His equations have now been modified to include the additional variables referred to above, and in consequence negative temperature coefficients of thermal conductivity have been calculated. These are in better agreement with the experimental values of the present paper.

The new equations, representing the latest development of the film hypothesis, contain all the variables required in a general hydrodynamical theory of convection. Even in a film theory hydrodynamical considerations seem unavoidable, since the size and characteristics of the film need to be explained.

XCVII. *Photoelectric and Photochemical Activity.* By O. W. RICHARDSON, F.R.S., *Wheatstone Professor of Physics, King's College, London*.*

THE formulæ developed by Kramers† and Milne‡ for the photoelectric activity of radiation in recent important papers have a very close connexion with formulæ which I obtained in 1911–13§ based, broadly speaking, on the same general type of ideas. The special features which link up the new formulæ with Bohr's theory are, of course, absent from mine, which originated independently of that theory and for the most part prior to the publication of it. The important formula is that expressed in equation (20), p. 224, of Milne's paper, which is the same as equation (17), p. 843, of Kramers. This is

$$\psi^{(r)}(\nu) = \frac{4\pi^2 m^2 \sigma v^2 F^{(r)}(v)}{q_r c} \left(\frac{c}{h\nu} \right)^3 = \frac{8\pi^2 \sigma m c^2 F^{(r)}(v)}{q_r} \frac{h\nu - \chi^{(r)}}{h^3 \nu^3}, \quad (1)$$

where $\psi^{(r)}(\nu)$ denotes the probability that an electron in the r th stationary state will be ejected from an atom in unit time by unit intensity of temperature radiation in the stretch ν to $\nu + d\nu$; q_r is the weight and σ the symmetry number of an electron in the r th state; $\chi^{(r)}$ is the corresponding ionization potential; and m , c , and h have their usual significance. $F^{(r)}(v)$ is the effective area of the appropriately ionized atom for capturing electrons moving with initial velocity v .

Let us compare this with the equation (5a) on p. 571 of *Phil. Mag.* Oct. 1912, which I give for a closely-related quantity, viz:—

$$\epsilon F(\nu) = \frac{A_1 h}{R^2 \nu^2} \left(1 - \frac{w_0}{h\nu} \right) = \text{const.} \times \frac{h\nu - \chi}{h^3 \nu^3} \dots \dots (2)$$

Here $\epsilon F(\nu)$ is the number of electrons emitted from unit area of a body having a single threshold given by $\chi = h\nu_0$

* Communicated by the Author.

† *Phil. Mag.* xlv. p. 836 (1923).

‡ *Phil. Mag.* xlvii. p. 209 (1924).

§ *Phil. Mag.* xxiii. p. 594 (1912), xxiv. p. 570 (1912), xxvii. p. 476 (1914).

per unit time per unit intensity of temperature radiation in the stretch ν to $\nu + d\nu$. The constant is independent of ν , v , T , and χ .

Equation (1) merges into (2), provided $F^{(v)}(v)$ is independent of v , or ν , of which it is in general a function through v . Now, the deduction of equation (2) involves the explicit assumption either that the proportion of the returning electrons which is reflected may be treated as negligible, or, if not negligible, at any rate independent of the temperature. Now, the temperature is proportional to the average value of $\frac{1}{2}mv^2$; so that either of these assumptions is equivalent to making the effective areas of the atoms for capturing electrons independent of v . This result is a direct consequence of the index 2 of T in equation (5) of the above paper, viz :—

$$\int_0^{\infty} \epsilon F(\nu) h\nu^3 e^{-\frac{h\nu}{RT}} d\nu = A_1 T^2 e^{-\frac{w_0}{RT}} \dots \dots \dots (3)$$

If, however, we do not assume that the proportion of electron reflexions is independent of the temperature, but make other assumptions about the behaviour of this phenomenon, we arrive at quite different results, as can be seen by the general method which is developed more fully in *Phil. Mag.* vol. xxvii. p. 476 (1914). We may, for example, assume that the probability of a capture is inversely proportional to the square of the velocity (or to the equivalent quantity $h\nu - \chi$.) This is the assumption which Milne requires to account for the finite absorption in the region of the continuous spectrum just beyond the limits of spectral series, and which Eddington has shown is consistent with the limiting value for small velocities under the inverse square law of attractions. The equivalent assumption in the notation in which I was operating is that the quantity α in equation (2) of *Phil. Mag.* p. 570, vol. xxiv. (1912), which is the proportion of the returning electrons which are absorbed (not reflected), should vary as T^{-1} . This has the effect of altering the index 2 of T in equation (3) above to 1, with the result that, instead of (3), we have

$$\int_0^{\infty} \epsilon F(\nu) h\nu^3 e^{-\frac{h\nu}{RT}} d\nu = \text{const.} \times T e^{-\frac{w_0}{RT}} \dots \dots \dots (4)$$

The solution of this by the same method is

$$\epsilon F(\nu) = 0, \quad 0 < h\nu < w_0, \quad \dots \dots (5)$$

$$\epsilon F(\nu) = \text{const.}/\nu^3, \quad w_0 < h\nu < \infty, \quad \dots \dots (6)$$

in agreement with Milne and Eddington for this case.

XCVIII. *Some Remarks on the Theory of Solutions.* By ANGUS F. CORE, *Chemical Department, The University, Manchester* *.

THE complete behaviour of a solution can only be deduced by a thorough application of statistical mechanical principles. Such a calculation would involve an exact knowledge of the interaction of the various species of molecule, and would in general be exceedingly complex. In default of such complete knowledge and analytical skill, progress has sometimes been attempted in the following way. The solute molecules have been considered as a gas, the complex interaction between the solute and solute, solute and solvent, and solvent and solvent molecules being for this purpose allowed for, necessarily somewhat roughly, by ascribing to the solute molecules alone an appropriate interaction, while the solvent is treated as a vacuum. The osmotic pressure of the solute is then deduced by calculating the external pressure of such a gas. The validity of this method was attacked by Mr. Cavanagh in the first of three articles on "Molecular Thermodynamics" (*Phil. Mag.* March 1922, p. 606). In the present paper it is sought to justify the "gas method" under certain conditions.

In the set of papers referred to, Mr. Cavanagh has elaborated an extension of Planck's thermodynamic method in his treatment of solutions. In this the thermodynamic potential of the solution is calculated in terms of the total energy and volume expressed as functions of the temperature, pressure, and composition. Mr. Cavanagh uses as components the various actual molecular species. If a knowledge of the properties of these molecules is presupposed, it might be possible to calculate the total energy and volume, and then, applying the thermodynamical relations, deduce the actual behaviour of the solution. Thus theory and experiment are brought into contact. The suggestion is made that, by measuring the colligative properties of the solutions of certain solutes in associating solvents, the degree of association of the solvent may be determined. An attempt is made in the present paper to show that this is not possible. The general question is raised as to the suitability of making the total energy and volume the connecting link between theory and experiment, and it is suggested that the use

* Communicated by Prof. S. Chapman.

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of the activities or "fugacities" * of the components is preferable.

1. Consider a solution contained in a vessel. At any instant the solute molecules are in a definite statistical arrangement with respect to each other. We may now imagine a gas occupying an equal volume and containing the same number of molecules as solute molecules in the solution and at the same temperature. If the intermolecular actions of the gas molecules are such that at any instant their statistical arrangement is the same as that of the solute molecules, then we may define the gas as equivalent to the solute for the particular concentration, the solution being at a given temperature and under a given hydrostatic pressure. The actual forces experienced by a single solute molecule at any instant when the other solute molecules are in given positions will be quite different from the forces experienced by an equivalent gas molecule similarly situated with respect to the other gas molecules. These forces are equivalent to the statistical average effect on the solute molecule so situated for all the possible positions of the solvent molecules, the other solute molecules remaining in the given positions.

Now suppose that we increase the concentration and adjust the hydrostatic pressure on the solution so that it remains in osmotic equilibrium with pure solvent at constant pressure. If under these conditions the same gas molecules remain equivalent to the solute, it will be shown that the osmotic pressure of the solute must equal the pressure exerted by the equivalent gas for all concentrations at the given temperature.

Consider a gas contained in a large vessel to which is attached a second vessel separated from the first by a partition of such a nature that when a gas molecule crosses the partition into the second vessel an amount of work χ is expended. Then χ is the mechanical potential of the region

* If " f " is the fugacity of a component in a given molecular state in one system and " f' " its fugacity in another system at the same temperature, then the work required to transfer some of the component from the first system to the second isothermally and under conditions of constant pressure is equal to $RT \log f'/f$ per gram molecule. This, together with the statement that the fugacity of the isolated component in the given molecular condition and in the state of a gas is equal to the gas-pressure, completes the definition of fugacity. It is evident that the fugacity of a molecular species in a liquid mixture is equal to the vapour-pressure of the corresponding molecules if the vapour behaves as a perfect gas.

in the second vessel. We shall suppose that χ is so great that at the temperature of the gas the concentration of molecules, ν_1 , across the partition is sufficiently small for the gas to behave perfectly. Now let there be a similar arrangement containing the gas at a slightly different concentration, and let ν_2 be the concentration in the high-potential region. Then the work required to transfer the

gas from the one system to the other is $RT \log \frac{\nu_2}{\nu_1}$ per gram

molecule. If C and $C+dC$, p and $p+dp$ are the concentrations and pressures in the two large vessels, then the work is also equal to dp/C per gram molecule. Therefore

$$\frac{\partial p}{\partial C} = RT \frac{\partial \log \nu}{\partial \log C}.$$

Now consider two exactly similar arrangements containing solutions of concentrations C and $C+dC$ and osmotic pressures π and $\pi+d\pi$, both in osmotic equilibrium with pure solvent at the same pressure. In this case, suppose that the partitions allow solvent to pass through perfectly freely, but that a solute molecule requires the work χ to pass through them. Let ν_1' and ν_2' be the molecular concentrations in the high-potential vessels. These are so small that we may assume that the osmotic pressure of the solute obeys the perfect gas laws. Then the work required to transfer solute from the concentration C to the concentration $C+dC$ is equal to $RT \log \frac{\nu_2'}{\nu_1'}$ per gram molecule. This work also equals $d\pi/C$. Therefore

$$\frac{\partial \pi}{\partial C} = RT \frac{\partial \log \nu'}{\partial \log C}.$$

We may now show that $\nu' = \nu$. For suppose that there are n molecules in the gas system. Then at any instant $n-1$ of these molecules are in definite positions. Consider a small region, dv , outside the influence of any of these $n-1$ molecules at the instant. Then there is a certain chance that the remaining molecule lies in this small region. This may be written $P_0 dv$. dv is a region of zero potential and P_0 is the same in every such region. The chance that the molecule lies in a unit of volume of the region of very high potential, χ , is therefore $P_0 e^{-\chi/RT}$. The total molecular concentration in the high-potential vessel is therefore given by

$$\nu = n P_0 e^{-\chi/RT}.$$

If there are also n molecules of solute in the solution, and the concentration is the same as that of the equivalent gas, then, since the statistical distribution is identical, the chance of a given solute molecule being in a small volume dv , in free solvent, that is outside the influence of any of the other solute molecules, is also $P_0 dv$. Therefore the concentration in the high-potential region is given by

$$\nu' = nP_0 e^{-X/KT}.$$

Thus $\nu' = \nu$. It follows therefore that

$$\frac{\partial \pi}{\partial C} = \frac{\partial p}{\partial C}.$$

When C is very small, $\pi = p$. Therefore for all concentrations $\pi = p$.

We may identify the quantity nP_0 with the activity of the solute or gas.

The activity in these cases is defined so as to be equal to the actual concentration for very dilute conditions, and so that the work of transferring a gram molecule from a region of activity a to a region of activity a' is equal to $RT \log a'/a$. It will be perceived that both these conditions are satisfied by the quantity nP_0 . Thus the activity of the equivalent gas is equal to the activity of the solute at the same concentration.

The activity of the solute as measured above is not quite equivalent to what is usually recorded as the activity of a solute. The difference in the logarithms of the activities of two solutions is usually identified with the work required to transfer a gram molecule of solute from the one solution to the other when the hydrostatic pressure on the solutions is the same. The activities we have considered refer to solutions maintained in equilibrium with free solvent at constant hydrostatic pressure. It seems to the writer that, from the point of view of theory, this is a more fundamental and more useful quantity, since its changes are not complicated by simultaneous changes in the potential of the free solvent.

The equality of p and π may be proved, perhaps, more directly as follows. Imagine parallel columns of the equivalent gas and solution in a vertical field of force. We may postulate that the field acts directly on the solute molecules and not on the solvent molecules; and that it acts with the same force on each gas molecule as it does on a single solute molecule. Suppose that the solution is limited below by a semi-permeable partition, beneath which is pure

solvent at a uniform pressure P in osmotic equilibrium with the solution. The columns of solution and gas are indefinitely extended in the upward direction. Let n be the number of solute molecules per unit area in the column above the semi-permeable partition, and let f be the force on each solute molecule exerted by the external field. The total force exerted by the field on the solution is therefore nf . Now raise the partition through a small vertical distance δx . The change effected by this is equivalent to raising the whole solution by δx and simultaneously transferring a certain quantity of solvent from a great height to the region under the partition. The work done therefore by this change against the external field is $n\delta x$ per unit area of the column. If π is the osmotic pressure just above the partition, the work done by the displacement is $\pi\delta x$ per unit area. Equating these two quantities, we obtain the relation $\pi = nf$. Similarly, if n' is the number of gas molecules per unit area above a level where the gas-pressure is p , then $p = n'f$. Now suppose that the gas is equivalent to the solute at all concentrations in solutions maintained in osmotic equilibrium with pure solvent at pressure P . Then, since the vertical column of solution is everywhere in equilibrium with pure solvent under a pressure P , it follows that the gas molecules will distribute themselves in exactly the same way as the solute molecules in the vertical field of force. Consequently $n' = n$. Therefore $\pi = p$.

The necessary and sufficient condition that this equality should hold is, then, that the same gas molecules should remain equivalent to the solute molecules for all concentrations of the solution when the hydrostatic pressure on the solution is adjusted so as to maintain the solution always in equilibrium with pure solvent under constant pressure. It is evident that no restriction is placed on the variation of the equivalent gas molecules with temperature, or on the variation of the volume of the solvent with temperature or pressure. It should be pointed out that this argument has no bearing on the "bombardment" theory of osmotic pressure. Whether the actual force on the membrane is the result of collisions with the solute molecules or not is of secondary importance, and must depend on the nature of the particular membrane used.

2. It is only in one or two very special cases that it is possible to say directly what is the approximate nature of the gas molecules which are equivalent to the solute molecules and so reduce the deduction of the osmotic pressure to

a problem in the kinetic theory of gases. It is sometimes supposed that the ions of a strong electrolyte behave in solution as though they acted on each other with forces varying inversely as the square of the distance between them. Although this assumption cannot be correct since it neglects the finite size of the solute and solvent molecules, nevertheless it is probably justifiable in the case of very dilute solutions. For these effects give rise to terms in the colligative properties of the solution which are proportional to a higher power of the concentration of the solute than that in the terms due to the electrostatic forces. The equivalent gas, then, consists of positively and negatively charged point molecules. If ϵ is the magnitude of the charge on each particle, the repulsion between two particles separated by a distance r is $+$ or $-\epsilon^2/Kr^2$ according to whether the particles have the same or opposite charges. K corresponds to the dielectric constant, and may be a function of the temperature without invalidating the method, but it must remain constant when the concentration of the solution is altered so long as this is maintained in osmotic equilibrium with pure solvent under constant pressure. If this is the case, we shall obtain the osmotic pressure of the electrolyte by calculating the pressure exerted by this equivalent gas. This may be done by calculating the activity of the gas or its virial, or, less naturally, by calculating the energy and applying the thermodynamic relation

$$p = T \int \frac{1}{T} \frac{\partial^2 U}{\partial v \partial T} dT - \left(\frac{\partial U}{\partial v} \right)_T.$$

In the integration there will occur a constant which gives rise to a term proportional to the temperature and to some function of the concentration. This term is equal to RT/v in the case of point molecules. In the integration the dielectric constant must be treated as independent of the temperature, even if in the solution it changes with the temperature.

Milner has calculated the virial of a gas consisting of point charges, and then obtained the pressure from the relation

$$pv = RT + \frac{1}{3}W.$$

In this, W is the virial and $1/v$ equals C , the total concentration of molecules of both signs. When the concentration is small,

$$W = -BC^{\frac{1}{2}},$$

and therefore

$$\pi = p = RTC - \frac{1}{3}BC^{\frac{3}{2}}.$$

In these

$$B = a\epsilon^3/R^{\frac{1}{2}}K^{\frac{3}{2}}T^{\frac{1}{2}},$$

“ a ” being a numerical constant.

An interesting case may be imagined in which the solute molecules are very large in comparison with the solvent molecules. In the liquid state the interaction between the different molecules may be such that over a wide range of temperature one solute molecule does not influence another solute molecule unless the distance between them is small compared with their linear dimensions. If the solute molecules are spherical and hard the equivalent gas will consist of hard non-attracting spheres. Therefore the osmotic pressure of the solute is given by

$$\pi = RTC + RTbC^2,$$

omitting terms proportional to a higher power of the concentration than the second. In this, b is equal to four times the actual volume of the molecules in a gram molecule of the solute. In this case the heat of dilution and the change of volume on dilution may be very slight, and yet Raoult's law of vapour-pressure will not be followed*.

3. We now turn to the thermodynamical treatment of solutions based on Planck's method. Consider for simplicity a mixture consisting of two molecular species only. Suppose that there are n_1 gram molecules of the first component and n_2 of the second. Let U be the total energy and V the total volume of the mixture. Then for the pure component 1 we may write

$$U = n_1 u_1, \quad V = n_1 v_1,$$

in which u_1 and v_1 depend on the temperature and pressure only. Now if we add a very little of component 2 so that

* All that is required here is that such a state of affairs should be possible. Nevertheless, to prevent possible misunderstanding, it may be pointed out that it is not at all a probable condition. However large a molecule is, it is still only a single molecule, and therefore, in order that the influence of one solute molecule on another should be negligible, it is necessary that the potential of the effective forces between them should be small compared with kT , k being the gas constant for a single molecule. The changes of potential energy associated with the variation of the modification in the solvent as two large solute molecules approach each other will probably be very far from small compared with kT , even when they are separated by a distance which is not small compared with their linear dimensions.

n_2 is very small compared with n_1 , we may assume that the following linear relation holds :

$$U = n_1 u_1 + n_2 u_2 ; \quad V = n_1 v_1 + n_2 v_2.$$

In these u_2 and v_2 are independent of everything except the temperature and pressure. These linear relations will be followed in all states of the mixture, gaseous or liquid. When the concentration of 2 is not very small, it is necessary to add extra terms to these expressions. Assume that it is possible to write them in the very general form* :

$$U = n_1 u_1 + n_2 u_2 + n_1 \sum u'_x f_x(c),$$

$$V = n_1 v_1 + n_2 v_2 + n_1 \sum v'_x f_x(c).$$

In these expressions c is written for n_2/n_1 . u' and v' depend only on the temperature and pressure, and $f_x(c)$ only on the composition. We may now calculate the Planck potential function

$$\psi = -(U + PV)/T + \int (dU + PdV)/T + \text{a constant.}$$

Suppose that the integration is carried out under conditions of constant composition. The constant is then independent of the temperature and pressure, and is some function of the composition. To evaluate this constant we may start with the mixture when very rarefied and at a high temperature, in which state it will approximate to a perfect gas mixture, and then, by changing the temperature and pressure, convert the gas continuously into the liquid condition at the required temperature and pressure. We may then write,

$$\psi = \psi_{\text{gas}} - \left[(U + PV)/T \right]_{\text{gas}}^{\text{liquid}} + \int_{\text{gas}}^{\text{liquid}} (dU + PdV)/T.$$

Now let

$$\phi_1 = -(u_1 + Pv_1)/T + \int (du_1 + Pd v_1)/T + l_1,$$

$$\phi_2 = -(u_2 + Pv_2)/T + \int (du_2 + Pd v_2)/T + l_2,$$

$$\phi'_x = -(u'_x + Pv'_x)/T + \int_{\text{gas}}^{\text{liquid}} (du'_x + Pd v'_x)/T.$$

* Cavanagh, "Molecular Thermodynamics," Phil. Mag. xliii. p. 606 (1922).

In these expressions l_1 and l_2 are independent of both temperature and pressure, and also of the composition of the mixture. For the gas state the value of ψ is given by

$$\psi_{\text{gas}} = n_1\phi_1 + n_2\phi_2 - Rn_1 \log \frac{n_1}{n_1 + n_2} - Rn_2 \log \frac{n_2}{n_1 + n_2}.$$

Therefore in the liquid state we may write

$$\psi = n_1\{\phi_1 + R \log (1+c)\} + n_2\left\{\phi_2 + R \log \frac{c}{1+c}\right\} + n_1 \Sigma \phi_x' f_x(c).$$

From this we may deduce the osmotic pressure. For moderately small values of c the osmotic pressure of component 2 is given by

$$\pi = \frac{T}{v_1} \left\{ R \log (1+c) + \Sigma \phi_x' \left(f_x(c) - c \frac{\partial f_x(c)}{\partial c} \right) \right\}.$$

Suppose now that the solute is a strong electrolyte. According to the theory of complete ionization, the electrostatic forces will give rise to a term in the osmotic pressure when the solution is very dilute proportional to the concentration to the power of $3/2$. For very dilute solutions we may therefore neglect terms involving higher powers of c . Only to this degree of approximation may we assume that the "extra" terms in the expression for the potential are fully represented by the electrostatic effect. To this degree of approximation Milner showed that the electrostatic energy of the ions is given by

$$E = -BC^{\frac{3}{2}},$$

in which, as before,

$$B = a\epsilon^3/R^{\frac{1}{2}}K^{\frac{3}{2}}T^{\frac{1}{2}}.$$

In this particular case the electrostatic energy is equal to the virial. C is the ordinary volume concentration. In terms of the concentration c , that is n_2/n_1 , this becomes to the necessary degree of approximation

$$E = -Bv_1^{-\frac{1}{2}}c^{\frac{3}{2}}.$$

This is the electrostatic energy per gram molecule. We shall first assume that the dielectric constant, K , and the molecular volume v_1 , are independent of the temperature. If this is so, the total energy of the solution may be written

$$U = n_1u_1 + n_2u_2 - n_1Bv_1^{-\frac{1}{2}}c^{\frac{3}{2}}.$$

It is also assumed that for all conditions

$$V = n_1 v_1 + n_2 v_2.$$

If these values be substituted in the relation given above, we obtain for the osmotic pressure to the required degree of approximation

$$\pi = RTF(c) - \frac{1}{3} B v_1^{-\frac{3}{2}} c^{\frac{3}{2}}.$$

When the charges on the ions are reduced to zero, then to the same approximation the osmotic pressure becomes RTc/v_1 . Therefore $F(c) = Rc/v_1$, and

$$\pi = RT v_1^{-1} c - \frac{1}{3} B v_1^{-\frac{3}{2}} c^{\frac{3}{2}}.$$

In terms of the volume concentration C , this becomes

$$\pi = RTC - \frac{1}{3} B C^{\frac{3}{2}}.$$

This necessarily agrees with the result obtained by calculating the pressure of the equivalent gas consisting of charged point molecules.

In the above deduction, K and v_1 were treated as independent of the temperature. If we had used the same value for the total energy and allowed for dK/dT and dv_1/dT , a different result would have been obtained for the osmotic pressure. But, as we have seen, it should be the same, for when calculated from the pressure of the equivalent gas, the result is independent of the variation of K and v_1 with the temperature. The explanation of this is that, when K and v_1 vary with the temperature, it is incorrect to suppose that the total energy of the solution is obtained by adding the electrostatic potential energy of the ions, calculated as if K and v_1 were constant, to the total energy which would exist apart from the charges on the ions.

Consider two small bodies, each carrying the charge e , at a distance r from each other in a medium of dielectric constant K . The potential energy is $-\epsilon^2/Kr$. If the bodies move so that the distance between them increases by δr , and if the volume of the medium is independent of r , then the "maximum work" of the change is given by

$$A = -\epsilon^2 \delta r / K r^2.$$

If K is independent of the temperature, then $-A = \delta U$, the change in the total energy U . If K varies with the temperature, then heat will be evolved or absorbed during the displacement of the charges and A will not equal $-\delta U$.

The thermodynamic relation is

$$\delta U = T^2 \left(\frac{\partial A/T}{\partial T} \right)_{\delta r}.$$

Therefore in this case

$$U = B - \frac{\epsilon^2}{K r} \left(1 - \frac{\partial \log K}{\partial \log T} \right),$$

where B is some quantity independent of r . The change in the last term during an isothermal change represents the heat evolved or absorbed from the medium.

In order to calculate the total energy of the electrolytic solution, consider the maximum work of transferring δn_1 gram molecules of solvent from the solution of composition n_1, n_2 to the pure solvent under the same pressure. If the solution is incompressible, this is given by

$$A = -\pi v_1 \delta n_1.$$

Substituting this in the relation between A and δU , and using the value of the osmotic pressure equal to the pressure of the equivalent gas, we obtain

$$U = n_1 u_1 + n_2 u_2 - n_1 B v_1^{-\frac{1}{2}} c^{\frac{3}{2}} \left(1 - \frac{1}{3} \frac{\partial \log K^3 v_1}{\partial \log T} \right).$$

Mr. Cavanagh seeks to disprove the validity of the "virial method" in his first paper. He considers an imaginary case in which the virial is proportional to $c^{\frac{1}{2}}$, and assumes that the extra energy of the solution due to the charges on the ions is then equal to the virial. Comparing the osmotic pressure obtained with this assumption with that obtained from the virial, certain impossible consequences follow. The virial of a gas is, however, equal to the potential energy only in the case when the forces between the molecules varies inversely as the square of the distance, and in that case when sufficiently rarefied it is proportional to $C^{\frac{1}{2}}$ and not to $C^{\frac{3}{2}}$. Moreover, as we have just seen, the extra energy of the solution which is to be used in the calculation of the thermodynamic potential equals the electrostatic potential energy of the ions only if the dielectric constant and the gram molecular volume of the solvent are independent of the temperature.

In the same paper Mr. Cavanagh proposes a method for estimating the degree of association of a solvent by measuring the colligative properties of a solution. Without affecting the argument, we shall assume that this is the

osmotic pressure of the solution. The measurement of the solubility of a gas is the experiment actually proposed. The use of a "perfect" solute is essential to the method.

In a very dilute solution for all conditions whether liquid or gaseous, we may assume that

$$U = n_1 u_1 + n_2 u_2,$$

$$V = n_1 v_1 + n_2 v_2.$$

All the quantities $f_x(c)$ are negligible. Planck's potential function is therefore given by

$$\psi = n_1 \phi_1 + n_2 \phi_2 - R n_1 \log \frac{n_1}{n_1 + n_2} - R n_2 \log \frac{n_2}{n_1 + n_2}.$$

From this we may deduce the colligative properties. In particular the osmotic pressure

$$\pi = \frac{RT}{v_1} \log \left(1 + \frac{n_2}{n_1} \right).$$

It is evident that we have no right to use any term involving a higher power of the composition than the first. The above expression is, therefore, equivalent to

$$\pi = \frac{RT}{v_1} \frac{n_2}{n_1}.$$

This is essentially Planck's treatment in his thermodynamics. Everything depends on the necessity for the linear relationship of U and V with the composition. Now suppose that even for more concentrated solutions this linear relation holds for all conditions of the mixture from that of a liquid. Then for incompressible solutions we should have accurately within the range of concentration for which the linear relation holds

$$\pi = \frac{RT}{v_1} \log \left(1 + \frac{n_2}{n_1} \right).$$

In this case the mixture is called a perfect one. As far as terms of the second order, this may be written

$$\pi = RTC + RT(v_2 - \frac{1}{2}v_1)c^2.$$

In this expression, C is the ordinary volume concentration. If the solvent consists of several molecular species, and if the energy and volume relations are linear in respect of the molecular concentration of the solute, then it is shown that for moderately small concentrations

$$\pi = RTC + RT(v_2 - \frac{1}{2}\bar{v}_1)c^2,$$

even if the equilibrium between the solvent species is

influenced by the presence of the solute. In this expression \bar{v}_1 is equal to \bar{m}_1/ρ , \bar{m}_1 being the average molecular weight of the solvent and ρ its density. It is therefore evident that if we were in possession of a guaranteed perfect solute, then by measuring π we could deduce the value of \bar{m} and therefore the degree of association of the solvent. But a perfect solute can only occur when very special conditions are fulfilled. When the two components of a binary mixture are exactly alike, they must certainly form a perfect mixture; the expressions for U and V must be linear with respect to n_1 and n_2 under all conditions. A mixture of two isotopes practically fulfils this condition unless, perhaps, when the temperature is very low. When the components are like each other, as in the case of benzene and toluene, a close approximation to a perfect mixture results. For a nearly perfect mixture the heat of dilution and the change of volume on dilution with either component must be very small over a wide range of temperature. It is important to notice that the converse of this is not necessarily true. The linearity of U and V with respect to n_1 and n_2 may be nearly true in the liquid condition, but not throughout all the stages between the gas condition and the liquid condition. In that case the liquid will not behave as a perfect mixture. The value of the integral

$$\Sigma \int_{\text{gas}}^{\text{liquid}} (du_x' + Pdv_x')/T$$

is not zero, but an unknown constant. This will give rise to a term in the osmotic pressure which is proportional to the temperature and to some probably complex function of the concentration. An ideal example of this is that of the large spherical solute molecules considered previously. In a general way it may be said that such cases occur if, while a certain balance exists between the attractions of solute for solute, solute for solvent, and solvent for solvent, yet the volume occupied by a solute molecule is very different from that occupied by a solvent molecule.

Suppose it was found in the case of a certain binary liquid mixture that the osmotic pressure of one component for all compositions throughout the complete range could be expressed by the simple relation

$$\pi = \frac{RT}{v_1} \log \left(1 + k \frac{M_2}{M_1} \right),$$

in which M_1 and M_2 are the masses of the two components in

the mixture and k is a constant ; or that the other colligative properties of the solution followed the correspondingly simple laws. Then we could say with confidence that k is the ratio of the molecular weight of the two components as they occur in the mixture. Moreover, we should conclude that the degree of polymerization, if any existed, of either component remained constant throughout the complete range of composition. Suppose, however, that this simple behaviour is not observed throughout the whole range ; and such behaviour would seem to be impossible when one of the components is an associating substance such as water. Then when the solution is exceedingly dilute, the osmotic pressure is RTC . From this it is possible to deduce simply the association of the solute. As the concentration is increased, the osmotic pressure will diverge from this, but there is no reason whatsoever for supposing that the second-order correction term will approximate to that proper to the perfect mixture after allowing for solvation and association. For the perfect mixture it is $RT(v_2 - \frac{1}{2}v_1)C^2$; for the large spherical solute molecules considered before, it is $RTbC^2$. It is necessary to suppose that, unless the mixture behaves perfectly throughout, the term is a complex function of the parameters defining the two kinds of molecule concerned. Thus in cases where there is reason to suppose that there is no solvation of the solute molecules and also no direct action between these, as for example in the case of a gas like argon dissolved in water, it is not justifiable to assume that the second term is equal to $RT(v_2 - \frac{1}{2}v_1)C^2$, and then from this to deduce the degree of association of the solvent. These remarks apply even if the heat of dilution and volume change on dilution are small.

5. Planck's method of deducing the colligative properties of solutions has led sometimes to misunderstanding concerning the occurrence and nature of perfect mixtures and the factors which cause departure therefrom. It would appear to be preferable to start with the relation between the fugacity and the concentration. There is exactly the same necessity for asserting that the fugacity of a definite molecular species is proportional to the concentration for all states of the mixture in the limit as the dilution is indefinitely increased, as there is for asserting that the energy and volume expressions are linear with respect to the composition. The other properties can then be deduced very simply.

Attempts have been made to carry the calculation of the colligative properties of solutions of strong electrolytes to a

stage further than Milner carried it. Allowance has been made for the finite size of the ions in deducing the energy introduced by the electrostatic attractions between them. The potential function is then calculated from the expression

$$\psi = n_1 \{ \phi_1 + R \log(1 + c) \} + n_2 \left\{ \phi_2 + R \log \frac{c}{1 + c} \right\} + n_1 \sum \phi'_x f_x(c).$$

It is incorrect to assume that the last term is entirely accounted for by these electrostatic effects, so that if the charges were reduced to zero the solution would behave as a perfect one. For in taking account of the finite size of the ions, terms are introduced which involve the square of the concentration or higher powers. If the ions are as large as these theories demand, the departure from perfect behaviour may be appreciable even at moderate concentrations, quite apart from the electrostatic effects.

The foregoing points have been emphasized because they illustrate the disadvantages of using the relationship of the total energy and volume of a mixture with the composition as a starting-point for the thermodynamical treatment. The volume of a liquid solution is frequently very nearly linear with respect to the composition, and in certain cases the total energy is either linear or contains an extra term, which can be calculated approximately as in the case of a solution of a strong electrolyte. But, as we have seen, this is not sufficient whereby to calculate the properties of the solution. In the expression for the osmotic pressure a term nearly proportional to the temperature and to a possibly complex function of the concentration is not associated with any appreciable quantity in the energy expression of the solution, and cannot be calculated from an approximate value of the energy. The principal object of formulating a thermodynamical treatment of a mixture of molecular species is to enable us to join theory to experiment—to build a bridge between them, so that from the dynamical theory we can calculate the actual behaviour of the mixture. From the dynamical theory it would then appear proper to calculate the fugacities or activities directly rather than the total energy and volume. Moreover, the former can be readily deduced from experimental results, and in some cases measured directly.

Chemical Department,
The University, Manchester,
February 1924.

XCIX. *Calculations of the Potential Energy for some Atomic Models.* By IDA WOODWARD*.

THE atomic models which form the basis of the following calculations are chosen for their simplicity; they consist of a positive nucleus surrounded by layers of electrons at rest. These electrons are divided into groups, all members of a group being at equal, or nearly equal, distances from the nucleus, and the electrons of a group are said to form a layer. As the two electrons which lie nearest to the nucleus are more intimately connected with it than are the remaining electrons, they are considered with the nucleus; this combination, which is generally spoken of as the atom, is regarded as a positive point charge, the magnitude of which is equal to the sum of the charges on the remaining electrons. If the number of these electrons be n , the charge on the atom is ne , where e has its usual significance, and denotes the magnitude of the electronic charge. Such an atom has the atomic number $(n+2)$.

The electrons in each layer are supposed to be distributed with as much symmetry as is geometrically possible, and the work is much simplified by this consideration. All values between one and eight are given to n , and the values 12 and 22 are considered in addition. For $n=1, 2$, and 4, all the electrons are supposed to lie in one layer. For $n=3$, the case in which the electrons lie on a straight line is considered as well as that in which they form one layer. For $n=5, 6, 7$, and 8, two cases are considered—that in which the electrons form one layer, and that in which they form two. For $n=8$, alternative distributions in the layers are considered. For $n=12$, two cases are considered, in each of which the electrons lie in two layers: in one case each of these layers contains 6 electrons, in the other they contain 8 and 4 electrons respectively. For $n=22$, the electrons are supposed to lie in three layers, containing (i.) 8, 8, and 6 electrons, (ii.) 8, 12, and 2 electrons. The number of electrons in the inmost layer is given first.

On account of the complexity of the equations obtained, an approximate solution only was found in more complicated cases.

The law of force assumed was everywhere as follows:—

Between an atom and an electron, an attraction $Ee\left(\frac{1}{r^2} - \frac{c}{r^3}\right)$,

Between two electrons, a repulsion $\frac{e^2}{r^2}$,

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

where r is the distance between the charges under consideration, E the charge on the atom, and c an unknown quantity, constant for any particular atom.

The results show the comparative stability of various atomic models.

V is used throughout to denote the potential energy of the atom with its associated electrons.

I. Atom with one electron.

$$n=1, E=e.$$

There is here only one possible model.

Let a be the distance between the atom and the electron.

$$\begin{aligned} V &= -Ee \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\} \\ &= -e^2 \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\}. \end{aligned}$$

The condition for equilibrium is $\frac{dV}{da} = 0$.

$$\text{Hence} \quad a=c,$$

$$\text{and} \quad V = -\frac{e^2}{c} \times \frac{1}{2}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

II. Atom with two electrons.

$$n=2, E=2e.$$

Electrons and atom on the same straight line, the electrons being equidistant from the atom.

Let a = distance of electrons from atom.

$$\begin{aligned} V &= -2Ee \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\} + \frac{e^2}{2a} \\ &= -\frac{3.5e^2}{a} + \frac{2ce^2}{a^2}. \end{aligned}$$

The condition of equilibrium $\frac{dV}{da} = 0$ gives

$$3.5 = 4c/a.$$

$$\therefore a = 4c/3.5 = 1.143,$$

$$\begin{aligned} \text{and} \quad V &= \left\{ -\frac{(3.5)^2}{4c} + \frac{2(3.5)^2}{16c} \right\} e^2 \\ &= -1.53125 \cdot \frac{e^2}{c}. \quad . \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

III. *Atom with three electrons.*

$$n=3, E=3e.$$

(i.) *One layer.*—Electrons at corners of an equilateral triangle, atom at its centroid.

Distance of electron from atom = a .

$$V = -3e^2 \left\{ \frac{3}{a} - \frac{3c}{2a^2} \right\} + \frac{3}{2} \cdot \frac{2}{\sqrt{3}} \frac{e^2}{a}.$$

For equilibrium, $\frac{dV}{da} = 0$.

$$\therefore -\frac{7 \cdot 268}{a^2} + \frac{9c}{a^3} = 0,$$

$$\therefore \frac{c}{a} = .8076, \quad a = 1 \cdot 238c,$$

$$\text{and} \quad V = -\frac{e^2}{c} \times 2 \cdot 934. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(ii.) *Electrons and atom in one straight line.*

Atom at O, electrons at A, B, D.



Let OA = a , OB = b , OD = d .

$$V = -3e^2 \left\{ \frac{1}{a} + \frac{1}{b} + \frac{1}{d} - \frac{c}{2a^2} - \frac{c}{2b^2} - \frac{c}{2d^2} \right\} \\ + e^2 \left\{ \frac{1}{b+a} + \frac{1}{a+d} + \frac{1}{d-b} \right\}. \quad . \quad . \quad (4)$$

The conditions of equilibrium, $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial c} = 0$, give the equations

$$\frac{3}{a^2} - \frac{3c}{a^3} - \frac{1}{(a+b)^2} - \frac{1}{(a+d)^2} = 0, \quad . \quad . \quad . \quad (5)$$

$$\frac{3}{b^2} - \frac{3c}{b^3} - \frac{1}{(a+b)^2} + \frac{1}{(d-b)^2} = 0, \quad . \quad . \quad . \quad (6)$$

$$\frac{3}{d^2} - \frac{3c}{d^3} - \frac{1}{(a+d)^2} - \frac{1}{(d-b)^2} = 0. \quad . \quad . \quad . \quad (7)$$

Neglecting a/d and b/d , equation (7) gives $d = 3c$.

If we try the solution

$$a=(1+x)c, \quad b=(1+y)c, \quad d=3(1+z)c,$$

and neglect squares and higher powers of x , y , and z , we obtain the equations :

$$-10+105x+8y+3z=0, \quad . \quad . \quad . \quad (8)$$

$$x+14y-3z=0, \quad . \quad . \quad . \quad (9)$$

$$-26+9x-72y+147z=0. \quad . \quad . \quad . \quad (10)$$

Hence $x=.087, \quad y=.035, \quad z=.192,$

$$\text{and } \left. \begin{aligned} a &= 1.087c, \\ b &= 1.035c, \\ c &= 3.577c. \end{aligned} \right\} . \quad . \quad . \quad . \quad (11)$$

Substituting in (4), it is found that

$$V = -\frac{e^2}{c} \times 2.7868. \quad . \quad . \quad . \quad (12)$$

IV. Atom with four electrons.

$$n=4, \quad E=4e.$$

One layer.—Electrons at corners of a regular tetrahedron, atom at its centre of volume.

Distance of electrons from atom = a .

$$V = -4 \times 4e^2 \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\} + \frac{4}{2} \times \frac{3}{1.633a}. \quad . \quad (13)$$

The condition of equilibrium $\frac{dV}{da} = 0$ is

$$\frac{12.3256}{a^2} - \frac{16c}{a^3} = 0.$$

$$\therefore \quad \frac{c}{a} = .7704, \quad a = 1.298c, \quad . \quad . \quad . \quad (14)$$

$$\text{and } V = -\frac{e^2}{c} \times 4.748. \quad . \quad . \quad . \quad (15)$$

V. Atom with five electrons.

$$n=5, \quad E=5e.$$

(i.) *One layer.*—Three electrons at the corner of an equilateral triangle, the atom lying at its centroid ; two electrons at equal distances from the atom, on a line through it perpendicular to the plane of the triangle.

Distance of each of the three electrons from atom = a .

Distance of each of the two electrons from atom = b .

$$\frac{V}{e^2} = -5 \left\{ \frac{3}{a} + \frac{2}{b} - \frac{3c}{2a^2} - \frac{2c}{2b^2} \right\} + \frac{2 \times 3}{\sqrt{a^2 + b^2}} + \frac{1}{2b} + \frac{3 \times 2}{2\sqrt{3a}} \quad (16)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, give

$$\frac{13.268}{a^2} - \frac{6a}{(a^2 + b^2)^{3/2}} - \frac{15c}{a^3} = 0, \quad (17)$$

$$\frac{9.5}{b^2} - \frac{6b}{(a^2 + b^2)^{3/2}} - \frac{10c}{b^3} = 0. \quad (18)$$

Eliminating c , and putting $\frac{b}{a} = x$, we get

$$4.423 - 4.75x - \frac{(2 - 3x^4)}{(1 + x^2)^{3/2}} = 0. \quad (19)$$

A graphical solution of (19) gives

$$x = 1.026.$$

Hence we find $\frac{c}{b} = .7265$, $\frac{c}{a} = .7454$.

Therefore $a = 1.342c$, $b = 1.376c$, (20)

$$\text{and } V = -\frac{e^2}{c} \times 6.806. \quad (21)$$

(ii.) *Two layers.*—Atom at origin of Cartesian coordinates, electrons at $(0, 0, a)$, $(0, 0, d)$, $(0, b, -f)$, $(\pm \frac{\sqrt{3}}{2}b, -\frac{b}{2}, -f)$. This corresponds to a system in which four electrons lie at the corners of a tetrahedron, and the fifth on a line drawn from the atom to one corner of the tetrahedron and produced.

$$\begin{aligned} \frac{V}{e^2} = -5 \left\{ \frac{3}{\sqrt{b^2 + f^2}} - \frac{3c}{2(b^2 + f^2)} + \frac{1}{a} + \frac{1}{d} - \frac{c}{2a^2} - \frac{c}{2d^2} \right\} \\ + \frac{3}{2} \times \frac{2}{\sqrt{3}b} + \frac{3}{\sqrt{b^2 + (a+f)^2}} + \frac{3}{\sqrt{b^2 + (d+f)^2}} + \frac{1}{d-a}. \end{aligned} \quad (22)$$

The conditions of equilibrium $\frac{\partial V}{\partial a}=0$, $\frac{\partial V}{\partial b}=0$, $\frac{\partial V}{\partial d}=0$, $\frac{\partial V}{\partial f}=0$, give

$$\frac{15b}{(b^2+f^2)^{3/2}} - \frac{1.732}{b^2} - \frac{3b}{(b^2+(a+f)^2)^{3/2}} - \frac{3b}{(b^2+(d+f)^2)^{3/2}} - \frac{15c \cdot b}{(b^2+f^2)} = 0, \quad (23)$$

$$\frac{15f}{(b^2+f^2)^{3/2}} - \frac{3(a+f)}{(b^2+(a+f)^2)^{3/2}} - \frac{3(d+f)}{(b^2+(d+f)^2)^{3/2}} - \frac{15f \cdot c}{(b^2+f^2)^2} = 0, \quad (24)$$

$$\frac{5}{a^2} - \frac{3(a+f)}{(b^2+(a+f)^2)^{3/2}} + \frac{1}{(d-a)^2} - \frac{5c}{a^3} = 0, \quad (25)$$

$$\frac{5}{d^2} - \frac{3(d+f)}{(b^2+(d+f)^2)^{3/2}} - \frac{1}{(d-a)^2} - \frac{5c}{d^3} = 0. \quad (26)$$

Neglecting powers of a/d , b/d , f/d and putting $a=b$, we obtain an approximate solution which suggests the trial solution :

$$\begin{aligned} a/c &= 1.1(1+x), \\ b/c &= 1.1(1+y), \\ f/c &= .4(1+w), \\ d/c &= 5(1+z), \end{aligned}$$

where x , y , z , and w are supposed small and their squares and higher powers neglected.

Substituting in equations (23) to (26) and expanding, we get

$$\begin{aligned} -.1410 + .2222x + 1.4589y + .2371w + .01594z &= 0, \\ -.0838 + .0624x + .7144y + .3072w + .0562z &= 0, \\ -.2582 + 3.2284x + .7335y + .1772w - .1685z &= 0, \\ +.00055 - .03709x + .01157y + .0135w - .0553z &= 0. \end{aligned}$$

Hence $x=.031$, $y=.120$, $w=-.192$, $z=.002$.

Therefore $a=1.134c$, $b=1.232c$, $f=.322c$, $d=5.105c$,

$$\text{and } V = -\frac{e^2}{d} \times 6.6672. \quad (27)$$

The distances of the electrons from the atom are readily found to be

$$\left. \begin{array}{l} 1.273c \text{ (three electrons),} \\ 1.134c \text{ (one electron),} \\ 5.105c \text{ (one electron).} \end{array} \right\} \quad . \quad . \quad . \quad (28)$$

a result which shows the amount of distortion produced by the atom lying outside on the inner layer.

VI. Atom with six electrons.

$$n=6, E=6e.$$

(i.) *One layer.*—Atom at $(0, 0, 0)$, electrons at $(\pm a, 0, 0)$, $(0, \pm a, 0)$, $(0, 0, \pm a)$. The atom is at the centre, and the electrons are at the centres of the faces, of a cube of edge $2a$.

$$V = -36e^2 \left\{ \frac{1}{a} - \frac{c}{2a^2} \right\} + \frac{6}{2} \times \frac{3.328}{a} \cdot e^2. \quad . \quad . \quad (29)$$

The condition of equilibrium $\frac{dV}{da} = 0$ gives

$$\frac{c}{a} = \frac{13.008}{18}, \quad a = 1.385c. \quad . \quad . \quad . \quad (30)$$

$$\text{Hence} \quad V = -\frac{e^2}{c} \times 9.40. \quad . \quad . \quad . \quad (31)$$

(ii.) *Two layers.*—Four electrons in inner, two in outer layer. Atom at $(0, 0, 0)$, electrons at $(\pm a, 0, b)$, $(0, \pm a, -b)$, $(0, 0, \pm d)$. The inner electrons lie at the corners of a tetrahedron, distorted by the two electrons lying on lines joining the atom to the middle points of two non-intersecting edges of the tetrahedron.

$$\begin{aligned} \frac{V}{e^2} = & -6 \left\{ \frac{4}{\sqrt{a^2 + b^2}} - \frac{4c}{2(a^2 + b^2)} \right\} - 6 \left\{ \frac{2}{d} - \frac{2c}{2d^2} \right\} \\ & + 2 \left\{ \frac{1}{2a} + \frac{2}{\sqrt{2a^2 + 4b^2}} \right\} + \frac{1}{2d} + \frac{4}{\sqrt{a^2 + (d-b)^2}} \\ & \quad \quad \quad \frac{4}{\sqrt{a^2 + (d+b)^2}}. \quad . \quad . \quad (32) \end{aligned}$$

The conditions of equilibrium $\frac{\partial V}{\partial a}=0$, $\frac{\partial V}{\partial b}=0$, $\frac{\partial V}{\partial d}=0$ give

$$-\frac{24a}{(a^2+b^2)^{3/2}} + \frac{24ca}{(a^2+b^2)^2} + \frac{1}{a^2} + \frac{8a}{(2a^2+4b^2)^{3/2}} + \frac{4a}{(a^2+(d-b)^2)^{3/2}} + \frac{4a}{(a^2+(d+b)^2)^{3/2}} = 0, \quad (33)$$

$$-\frac{24b}{(a^2+b^2)^{3/2}} + \frac{24cb}{(a^2+b^2)^2} + \frac{16b}{(2a^2+4b^2)^{3/2}} - \frac{4(d-b)}{(a^2+(d-b)^2)^{3/2}} + \frac{4(d+b)}{(a^2+(d+b)^2)^{3/2}} = 0, \quad (34)$$

$$-\frac{23}{2d^2} + \frac{12c}{d^3} + \frac{4(d-b)}{(a^2+(d-b)^2)^{3/2}} + \frac{4(d+b)}{(a^2+(d+b)^2)^{3/2}} = 0. \quad (35)$$

An approximate solution, neglecting a/d and b/d , suggests the trial solution :

$$a=(1+x)c, \quad b=.6(1+y)c, \quad d=3.4(1+z)c.$$

Neglecting squares and higher powers of x , y , and z , equations (33), (34), (35) give

$$\begin{aligned} .0763 - 2.5120x - .8086y - .1572z &= 0, \\ .0050 - 1.0498x - .7799y - .5471z &= 0, \\ -.0089 - .04622x - .0223y - .6141z &= 0. \end{aligned}$$

$$\begin{aligned} \text{Hence} \quad x &= .04726, & y &= -.0366, & z &= .044, \\ \text{and} \quad a &= 1.047c, & b &= .5780c, & d &= 3.55c. \end{aligned}$$

$$\text{Therefore} \quad V = -\frac{e^2}{c} \times 8.868, \quad (36)$$

and the distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.196c \text{ (four electrons),} \\ 3.55c \text{ (two electrons).} \end{array} \right\} \quad (37)$$

VIII. Atom with seven electrons.

$$n=7, \quad E=7e.$$

(i.) *One layer.*—Five electrons at the corners of a regular pentagon, at the centre of which the atom lies, and two at equal distances from the atom on a line through it perpendicular to the pentagon.

Distance of each of the five electrons from the atom = a ,
 „ „ „ two „ „ „ = b .

$$V = -7e^2 \left\{ \frac{5}{a} - \frac{5c}{2a^2} + \frac{2}{b} - \frac{2c}{2b^2} \right\} + \frac{10}{\sqrt{a^2 + b^2}} + \frac{1}{2b} \\ + \frac{5}{2} \left\{ \frac{2}{a \cdot 2 \sin 36^\circ} + \frac{2}{a \cdot 2 \sin 72^\circ} \right\} \quad . \quad . \quad (38)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$ give

$$\frac{28 \cdot 1185}{a^2} - \frac{10a}{(a^2 + b^2)^{3/2}} - \frac{35c}{a^3} = 0, \quad . \quad . \quad (39)$$

$$\frac{13 \cdot 5}{b^2} - \frac{10b}{(a^2 + b^2)^{3/2}} - \frac{14c}{b^3} = 0. \quad . \quad . \quad (40)$$

Eliminating c and putting $\frac{a}{b} = x$, we get

$$56 \cdot 237x - 67 \cdot 5 - \frac{10(2x^4 - 5)}{(x^2 + 1)^{3/2}} = 0. \quad . \quad . \quad (41)$$

Solving graphically, it is found that $x = 1 \cdot 0496$.

$$\text{Hence} \quad \left. \begin{aligned} a &= 1 \cdot 4384c, \\ b &= 1 \cdot 3702c, \end{aligned} \right\} \quad . \quad . \quad . \quad (42)$$

$$\text{and} \quad V = -\frac{e^2}{c} \times 12 \cdot 185. \quad . \quad . \quad . \quad (43)$$

It is seen from (42) that two of the electrons are slightly nearer to the atom than the remaining five.

(ii.) *Two layers.*—Five electrons in inner, two in outer layer. Three of the electrons lie at the corners of an equilateral triangle, the atom at its centroid, and the remaining electrons on a line through the atom perpendicular to the plane of the triangle, and symmetrically disposed with regard to it.

Distance of three electrons from atom = a ,
 „ two „ „ „ = b , } inner layer.
 „ two „ „ „ = d , } outer layer.

$$\frac{V}{e^2} = -7 \left\{ \frac{3}{a} + \frac{2}{b} + \frac{2}{d} - \frac{3c}{2a^2} - \frac{2c}{2b^2} - \frac{2c}{2d^2} \right\} + \frac{3}{2} \times \frac{2}{\sqrt{3}a} \\ + \frac{2 \times 3}{\sqrt{a^2 + b^2}} + \frac{2 \times 3}{\sqrt{a^2 + d^2}} + \frac{2}{d-b} + \frac{2}{d+b} + \frac{1}{2b} + \frac{1}{2d}. \quad (44)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$ give

$$\frac{19.268}{a^2} - \frac{6a}{(a^2 + b^2)^{3/2}} - \frac{6a}{(a^2 + d^2)^{3/2}} - \frac{21c}{a^3} = 0, \quad (45)$$

$$\frac{13.5}{b^2} + \frac{2}{(d-b)^2} - \frac{2}{(d+b)^2} - \frac{6b}{(a^2 + b^2)^{3/2}} - \frac{14c}{b^3} = 0, \quad (46)$$

$$\frac{15.5}{d^2} + \frac{2}{(d-b)^2} - \frac{2}{(d+b)^2} - \frac{6d}{(a^2 + d^2)^{3/2}} - \frac{14c}{d^3} = 0. \quad (47)$$

An approximate solution, obtained by neglecting a/d and b/d , suggests the trial solution

$$a = 1.25(1+x)c, \quad b = 1.25(1+y)c, \quad d = 4(1+z)c,$$

where the squares and higher powers of x , y , and z are to be neglected.

Equations (45), (46), (47) give

$$.0313 + 2.1558x + .5434y + .0743z = 0,$$

$$.1541 + .8189x + 2.5847y - .3294z = 0,$$

$$-.01903 + .0435x - .1029y + .2070z = 0.$$

$$\text{Hence} \quad x = -.005, \quad y = -.047, \quad z = .079,$$

$$\left. \begin{aligned} \text{and} \quad a &= 1.244c, \\ b &= 1.191c, \\ d &= 4.316c. \end{aligned} \right\} \quad (48)$$

$$\text{Therefore} \quad V = -\frac{e^2}{c} \times 12.096. \quad (49)$$

(iii.)—*Two layers.* Six electrons in inner, one in outer layer. A number of arbitrary arrangements were studied, but the equilibrium position was not found on account of the complexity of the equations involved. If the positions of the electrons are given by $[a, 0, 0]$, $[g, \pm b, 0]$, $[g, 0, \pm b]$, $[-d, 0, 0]$, $[f, 0, 0]$, the atom being at the origin, then six of the electrons lie at the corners of an octahedron, and the remaining electron lies on a line joining the atom to one of the corners. This is an equilibrium distribution, but on account of the large number of unknown quantities involved, the solution would be very laborious.

The value of V is given by

$$\begin{aligned} \frac{V}{e^2} = & -7 \left\{ \frac{1}{a} + \frac{1}{d} + \frac{1}{f} + \frac{4}{\sqrt{b^2 + g^2}} - \frac{c}{2} \left(\frac{1}{a^2} + \frac{1}{d^2} + \frac{1}{f^2} \right. \right. \\ & \left. \left. + \frac{4}{b^2 + g^2} \right) \right\} + \frac{1}{f-a} + \frac{1}{f+d} + \frac{4}{\sqrt{(f-g)^2 + b^2}} + \frac{1}{a+d} \\ & + \frac{4}{\sqrt{(a-g)^2 + b^2}} + \frac{4}{\sqrt{(d+g)^2 + b^2}} + \frac{2}{2b} + \frac{4}{\sqrt{2} \cdot b}. \quad (50) \end{aligned}$$

Arbitrary values were assigned to a , b , d , f , and g , as follow:—

$$(A) \quad g=0, \quad a=b=d=1.3119c, \quad f=7c;$$

$$\therefore \quad V = -\frac{e^2}{c} \times 12.257. \quad \dots (51 A)$$

$$(B) \quad g=0, \quad a=b=d=1.3c, \quad f=7c;$$

$$\therefore \quad V = -\frac{e^2}{c} \times 12.2684. \quad \dots (51 B)$$

$$(C) \quad g=0, \quad a=d=1.352c, \quad b=1.267c, \quad f=6.93c;$$

$$\therefore \quad V = -\frac{e^2}{c} \times 12.6611. \quad \dots (51 C)$$

These arbitrary distributions give values of V less than those obtained for the two equilibrium positions studied, and show that those positions are not the most stable ones.

VIII. *Atom with eight electrons.*

$$n=8, \quad E=8e.$$

(i.) *One layer.*—Electrons at the corners of a cube of edge $2a$, atom at the centre of this cube.

$$\begin{aligned} \frac{V}{e^2} = & -8 \times 8 \left\{ \frac{1}{\sqrt{3}a} - \frac{c}{2 \times 3a^2} \right\} + \frac{8}{2} \left\{ \frac{3}{2a} + \frac{3}{2\sqrt{2} \cdot a} \right. \\ & \left. + \frac{1}{2\sqrt{3}a} \right\}. \quad (52) \end{aligned}$$

The condition of equilibrium $\frac{dV}{da} = 0$ gives

$$\frac{c}{a} = 1.198, \quad a = .8347c.$$

$$\text{Hence} \quad V = -\frac{e^2}{c} \times 15.28. \quad \dots (53)$$

The distance of the electrons from the atom

$$= \sqrt{3}a = 1.446c. \quad \dots (54)$$

(ii.) *One layer.*—Electrons at the corners of a twisted cube, atom at the centre of this figure. The coordinates of the electrons are $(\pm a, \pm a, +b)$, $(0, \pm \sqrt{2}a, -b)$, $(\pm \sqrt{2}a, 0, -b)$, and those of the atom $(0, 0, 0)$.

$$\frac{V}{e^2} = -64 \left\{ \frac{1}{\sqrt{2a^2 + b^2}} - \frac{c}{2(2a^2 + b^2)} \right\} + \frac{8}{2} \left\{ \frac{2}{2a} + \frac{2}{\sqrt{4a^2 + 4b^2 - 2\sqrt{2} \cdot a^2}} + \frac{2}{\sqrt{4a^2 + 4b^2 + 2\sqrt{2} \cdot a^2}} + \frac{1}{2\sqrt{2}a} \right\}. \quad (55)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$ and $\frac{\partial V}{\partial b} = 0$ give

$$\frac{16 \times 2a}{(2a^2 + b^2)^{3/2}} - \frac{8c \cdot 4a}{(2a^2 + b^2)^2} - \frac{1 \cdot 3536}{a^2} - \frac{2928a}{(2928a^2 + b^2)^{3/2}} - \frac{1 \cdot 7072a}{(1 \cdot 7072a^2 + b^2)^{3/2}} = 0. \quad (56)$$

$$\frac{16 \times b}{(2a^2 + b^2)^{3/2}} - \frac{8c \times 2b}{(2a^2 + b^2)^2} - \frac{b}{(2928a^2 + b^2)^{3/2}} - \frac{b}{(1 \cdot 7072a^2 + b^2)^{3/2}} = 0. \quad (57)$$

Eliminating c and putting $x = b/a$,

$$- \cdot 6768 + \frac{\cdot 8536}{(\cdot 2928 + x^2)^{3/2}} + \frac{\cdot 1464}{(1 \cdot 7072 + x^2)^{3/2}} = 0. \quad (58)$$

A graphical solution of (58) gives $x = \cdot 96$.

Hence $b = \cdot 8128c$ and $a = \cdot 8467c$.

$$\text{and} \quad V = -\frac{e^2}{c} \times 16 \cdot 75. \quad (59)$$

The distance of an electron from the atom

$$= \sqrt{2a^2 + b^2} = 1 \cdot 447c. \quad (60)$$

(iii.) *Two layers.*—Electrons at the corners of two similarly orientated regular tetrahedra. The edges of the tetrahedra are a and b respectively, where $a > b$.

$$\frac{V}{e^2} = 8 \times 4 \left\{ \frac{2\sqrt{2}}{\sqrt{3}a} - \frac{c \cdot 8}{2 \times 3a^2} \right\} - 8 \times 4 \left\{ \frac{2\sqrt{2}}{\sqrt{3}b} - \frac{c \times 8}{2 \times 3b^2} \right\} + \frac{4 \times 3}{2a} + \frac{4 \times 3}{2b} + 4 \left\{ \frac{2\sqrt{2}}{\sqrt{3}(a-b)} + \frac{3 \times 2 \times \sqrt{2}}{\sqrt{3a^2 + 3b^2 + 2ab}} \right\}. \quad (61)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$ and $\frac{\partial V}{\partial b} = 0$ give

$$11.57 - \frac{64c}{a^2} - \frac{2\sqrt{2}}{3a^3} - \frac{6\sqrt{2}(3a+b)}{\sqrt{3}(a-b)^2} - \frac{6\sqrt{2}(3a+b)}{(3a^2+3b^2+2ab)^{3/2}} = 0, \quad (62)$$

$$11.57 - \frac{64c}{b^2} - \frac{2\sqrt{2}}{3b^3} + \frac{2\sqrt{2}}{\sqrt{3}(a-b)^2} - \frac{6\sqrt{2}(3b+a)}{(3a^2+3b^2+2ab)^{3/2}} = 0. \quad (63)$$

Eliminating c and putting $a/b = x$, we get

$$11.57 - \frac{1.633(x^3+1)}{(x-1)^3} - \frac{8.485(x+1)(3x^2+x+3)}{(3x^2+2x+3)^{3/2}} = 0. \quad (64)$$

A graphical solution gives $x = 2.81$.

$$\begin{aligned} \text{Hence } b &= 1.808c, & a &= 5.083c, \\ \text{and } V &= -\frac{e^2}{c} \times 14.73. \end{aligned} \quad (65)$$

The distances of the electrons from the atom are

$$\left. \begin{aligned} 1.105c & \text{ (four electrons),} \\ 3.108c & \text{ (four electrons).} \end{aligned} \right\} \quad (66)$$

(iv.) *Two layers.*—Electrons at corners of two regular tetrahedra, placed so that each face of one is parallel to a face of the other, but on the opposite side of the atom. The distances of the electrons from the atom are a and b .

$$\begin{aligned} \frac{V}{e^2} &= -8 \left\{ \frac{4}{a} - \frac{4c}{2a^2} + \frac{4}{b} - \frac{4c}{2b^2} \right\} + \frac{3}{2} \times \frac{4\sqrt{3}}{2\sqrt{2}a} \\ &+ \frac{3}{2} \times \frac{4\sqrt{3}}{2\sqrt{3}b} \times 4 \left\{ \frac{1}{a+b} + \frac{3}{\sqrt{a^2 - \frac{2}{3}ab + b^2}} \right\} \end{aligned} \quad (67)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, give

$$\frac{28.326}{a^2} - \frac{32c}{a^3} - \frac{4}{(a+b)^2} - \frac{12(a-b/3)}{(a^2 - \frac{2}{3}ab + b^2)^{3/2}} = 0, \quad (68)$$

$$\frac{28.326}{b^2} - \frac{32c}{b^3} - \frac{4}{(a+b)^2} - \frac{12(-a/3+b)}{(a^2 - \frac{2}{3}ab + b^2)^{3/2}} = 0. \quad (69)$$

Eliminating c and putting $x = b/a$,

$$7.0815 - \frac{(1+x+x^2)}{(1+x)^2} - \frac{(1+x)(3x^2-x+3)}{(1-\frac{2}{3}x+x^2)^{3/2}} = 0. \quad (70)$$

A graphical solution gives $x=0.77$.

$$\text{Hence } \begin{cases} a=1.705c, \\ b=1.312c, \end{cases} \quad \dots \quad (71)$$

$$\text{and } V = -\frac{e^2}{c} \times 14.797. \quad \dots \quad (72)$$

(v.) *Two layers.*—Six electrons in inner layer, two in outer. Coordinates of electrons are $(\pm a, \pm a, 0)$, $(0, 0, \pm b)$, $(0, 0, \pm d)$, and those of the atom $(0, 0, 0)$. Four of the electrons are therefore at the corners of a square, the atom lying at its centre, and the remaining four lie symmetrically on a line through the atom perpendicular to the plane of the square.

$$\begin{aligned} \frac{V}{e^2} = & -8 \left\{ \frac{4}{\sqrt{2a}} + \frac{2}{b} + \frac{2}{d} - \left(2 \times \frac{c \cdot 4}{2a^2} + \frac{2c}{2b^2} + \frac{2c}{2d^2} \right) \right\} \\ & + \frac{4}{2} \left\{ \frac{1}{a} + \frac{1}{2\sqrt{2a}} + \frac{2}{\sqrt{2a^2+b^2}} + \frac{2}{\sqrt{2a^2+d^2}} \right\} + \frac{4}{\sqrt{2a^2+b^2}} \\ & + \frac{1}{d-b} + \frac{1}{d+b} + \frac{1}{2b} + \frac{4}{\sqrt{2a^2+d^2}} + \frac{1}{d-b} + \frac{1}{d+b} + \frac{1}{2d}. \end{aligned} \quad \dots \quad (73)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$, give

$$\frac{19.9232}{a^2} - \frac{16a}{(2a^2+b^2)^{3/2}} - \frac{16a}{(2a^2+d^2)^{3/2}} - \frac{16c}{a^3} = 0, \quad \dots \quad (74)$$

$$\frac{31}{2b^2} + \frac{2}{(d-b)^2} - \frac{2}{(d+b)^2} - \frac{8b}{(2a^2+b^2)^{3/2}} - \frac{16c}{b^3} = 0, \quad \dots \quad (75)$$

$$\frac{31}{2d^2} - \frac{2}{(d-b)^2} - \frac{2}{(d+b)^2} - \frac{8d}{(2a^2+d^2)^{3/2}} - \frac{16c}{d^3} = 0. \quad \dots \quad (76)$$

An approximate solution obtained by neglecting a/d and b/d suggests the trial solution

$$a=0.8(1+x)c, \quad b=1.2(1+y)c, \quad d=5(1+z)c,$$

where squares and higher powers of x , y , and z are to be neglected.

Equations (74), (75), (76) give approximately

$$-0.2301 + 2.7592x + 0.3540y + 0.0222z = 0,$$

$$-0.7304 + 3.0211x + 9.1286y - 0.2804z = 0,$$

$$+0.0046 + 0.0889x - 0.0673y + 0.1831z = 0.$$

$$\text{Hence } x=0.08, \quad y=0.056, \quad z=-0.04,$$

$$\text{and } a=0.864c, \quad b=1.267c, \quad d=4.80c.$$

Therefore
$$V = -\frac{e^2}{c} \times 16.052. \quad . \quad . \quad . \quad . \quad (77)$$

The distances of the electrons from the atoms are

$$\left. \begin{array}{l} 1.221c \text{ (four electrons),} \\ 1.267c \text{ (two electrons),} \\ 4.80c \text{ (two electrons).} \end{array} \right\} . \quad . \quad . \quad . \quad (78)$$

A more exact solution of the equations of equilibrium is given by

$$a = .909c, \quad b = 1.267c, \quad d = 4.80c.$$

This gives

$$V = -\frac{e^2}{c} \times 15.01, \quad . \quad . \quad . \quad . \quad (77 A)$$

and the distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.287c \text{ (four electrons),} \\ 1.267c \text{ (two electrons),} \\ 4.80c \text{ (two electrons).} \end{array} \right\} . \quad . \quad . \quad . \quad (78 A)$$

IX. *Atom with twelve electrons.*

$$n = 12, \quad E = 12e.$$

(i.) *Two layers.*—Six electrons in each layer. Coordinates of electrons are $(\pm a, 0, 0)$, $(0, \pm a, 0)$, $(0, 0, \pm a)$, $(\pm b, 0, 0)$, $(0, \pm b, 0)$, $(0, 0, \pm b)$, and of the atom $(0, 0, 0)$, where $b > a$.

$$\begin{aligned} \frac{V}{e^2} = & -72 \left\{ \frac{1}{a} - \frac{c}{2a^2} + \frac{1}{b} - \frac{c}{2b^2} \right\} + \frac{6}{2} \left\{ \frac{4}{\sqrt{2}a} + \frac{1}{2a} \right\} \\ & + \frac{6}{2} \left\{ \frac{4}{\sqrt{2}b} + \frac{1}{2b} \right\} + 6 \left\{ \frac{1}{b-a} + \frac{4}{\sqrt{a^2+b^2}} + \frac{1}{a+b} \right\}. \end{aligned} \quad (79)$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, give

$$\frac{24}{a^2} - \frac{24c}{a^3} - \frac{3.3288}{a^2} + \frac{2}{(b-a)^2} - \frac{8a}{(a^2+b^2)^{3/2}} - \frac{2}{(a+b)^2} = 0, \quad . \quad . \quad . \quad (80)$$

$$\frac{24}{b^2} - \frac{24c}{b^3} - \frac{3.3288}{b^2} - \frac{2}{(b-a)^2} - \frac{8b}{(a^2+b^2)^{3/2}} - \frac{2}{(a+b)^2} = 0. \quad . \quad . \quad . \quad (81)$$

Eliminating c and putting $x = b/a$,

$$10.3356 - \frac{(1+x^3)}{(x-1)^3} - \frac{4(1+x)}{(1+x^2)^{3/2}} - \frac{(1+x+x^2)}{(1+x)^2} = 0. \quad (82)$$

A graphical solution gives $x=2.65$.

$$\text{Hence } \left. \begin{aligned} a &= 1.148c, \\ b &= 3.042c, \end{aligned} \right\} \dots \dots \dots (83)$$

$$\text{and } V = -\frac{e^2}{c} \times 31.1976. \dots \dots \dots (84)$$

(ii.) *Two layers.*—Eight electrons in inner, four in outer layer. The electrons in the inner layer are supposed to lie at the corners of a cube; those in the outer at the corners of a tetrahedron, two edges of which are parallel to two edges of the cube. The coordinates of the electrons are $(\pm a, \pm a, \pm a)$, $(b, b, 2b)$, $(-b, -b, -2b)$, $(-b, +b, -2b)$, $(b, -b, -2b)$, and those of the atom $(0, 0, 0)$. The distortion of the cube on account of the atoms in the outer layer is neglected.

$$\begin{aligned} \frac{V}{e^2} = & -12 \left[8 \left\{ \frac{1}{\sqrt{3}a} - \frac{c}{2 \times 3a^2} \right\} + 4 \left\{ \frac{1}{\sqrt{6}b} - \frac{c}{2 \times 6b^2} \right\} \right] \\ & + \frac{1}{2} \left[8 \left\{ \frac{3}{2a} + \frac{3}{2\sqrt{2}a} + \frac{1}{2\sqrt{3}a} \right\} + 4 \left\{ \frac{1}{2\sqrt{2}b} + \frac{2}{2\sqrt{5}b} \right\} \right] \\ & + 4 \left[\frac{1}{\sqrt{2(b-a)^2 + (2b-a)^2}} + \frac{2}{\sqrt{(b-a)^2 + (b+a)^2 + (2b-a)^2}} \right. \\ & \quad \left. + \frac{1}{\sqrt{(b+a)^2 + (2b-a)^2}} \right. \\ & \quad \left. + \frac{1}{\sqrt{2(b-a)^2 + (2b+a)^2}} + \frac{2}{\sqrt{(b-a)^2 + (b+a)^2 + (2b+a)^2}} \right. \\ & \quad \left. + \frac{1}{\sqrt{2(b+a)^2 + (2b+a)^2}} \right] \dots (85) \end{aligned}$$

If we neglect squares and higher powers of a/b , this becomes

$$\begin{aligned} \frac{V}{e^2} = & -12 \left[\frac{8}{\sqrt{3}a} - \frac{8c}{2 \times 3a^2} + \frac{4}{\sqrt{6}b} - \frac{4c}{2 \times 6b^2} \right] \\ & + \frac{11.3976}{a} + \frac{1.6016}{b} + \frac{32}{\sqrt{6}b} \dots (86) \end{aligned}$$

The conditions of equilibrium $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, give

$$\frac{44.0328}{a^2} - \frac{32c}{a^3} = 0, \dots \dots \dots (87)$$

$$\frac{4.9312}{b^2} - \frac{8c}{b^3} = 0. \dots \dots \dots (88)$$

$$\text{Hence } a = .7267c, \quad b = 1.622c,$$

$$\text{and } V = -\frac{e^2}{c} \times 31.808. \dots \dots \dots (89)$$

The distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.258c \text{ (eight electrons), } \\ 3.973c \text{ (four electrons). } \end{array} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (90)$$

X. *Atom with twenty-two electrons.*

$$n=22, E=22e.$$

(i.) *Three layers.*—Eight, eight, and six electrons in the consecutive layers, starting from the inmost. Coordinates of electrons $(\pm a, \pm a, \pm a)$, $(\pm b, \pm b, \pm b)$, $(\pm d, 0, 0)$, $(0, \pm d, 0)$, $(0, 0, \pm d)$, and of atom $(0, 0, 0)$.

$$\begin{aligned} \frac{V}{e^2} = & -22 \left[8 \left\{ \frac{1}{\sqrt{3}a} - \frac{c}{2 \times 3a^2} \right\} + 8 \left\{ \frac{1}{\sqrt{3}b} - \frac{c}{2 \times 3b^2} \right\} \right. \\ & + 6 \left\{ \frac{1}{d} - \frac{c}{2d^2} \right\} \left. \right] + \frac{8}{2} \left\{ \frac{3}{2a} + \frac{3}{2\sqrt{2}a} + \frac{1}{2\sqrt{3}a} \right\} \\ & + \frac{8}{2} \left\{ \frac{3}{2b} + \frac{3}{2\sqrt{2}b} + \frac{1}{2\sqrt{3}b} \right\} + \frac{6}{2} \left\{ \frac{4}{\sqrt{2}d} + \frac{1}{2d} \right\} \\ & + 8 \left\{ \frac{1}{\sqrt{3}(a+b)} + \frac{3}{\sqrt{(a-b)^2 + 2(a+b)^2}} \right. \\ & + \left. \frac{3}{\sqrt{2(a-b)^2 + (a+b)^2}} + \frac{1}{\sqrt{3}(a+b)} \right\} \\ & + 6 \left\{ \frac{4}{\sqrt{(d-a)^2 + 2a^2}} + \frac{4}{\sqrt{(d+a)^2 + 2a^2}} \right\} \\ & + 6 \left\{ \frac{4}{\sqrt{(d-b)^2 + 2b^2}} + \frac{4}{\sqrt{(d+b)^2 + 2b^2}} \right\} \cdot \quad \cdot \quad \cdot \quad (91) \end{aligned}$$

The conditions of equilibrium are $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$.

If in these a/d and b/d are neglected, the following equations are obtained:—

$$\begin{aligned} \frac{90.2244}{a^2} - \frac{176c}{3a^3} + \frac{8}{\sqrt{3}(b-a)^2} - \frac{24(3a-b)}{(3a^2-2ab+3b^2)^{3/2}} \\ - \frac{24(3a+b)}{(3a^2+2ab+3b^2)^{3/2}} - \frac{8}{\sqrt{3}(a+b)^2} = 0, \quad \cdot \quad (92) \end{aligned}$$

$$\begin{aligned} \frac{90.2244}{b^2} - \frac{176c}{3b^3} - \frac{8}{\sqrt{3}(b-a)^2} + \frac{24(a-3b)}{(3a^2-2ab+3b^2)^{3/2}} \\ - \frac{24(a+3b)}{(3a^2+2ab+3b^2)^{3/2}} - \frac{8}{\sqrt{3}(a+b)^2} = 0, \quad \cdot \quad (93) \end{aligned}$$

$$\frac{122.0136}{d^2} - \frac{132c}{d^3} - \frac{96}{d^2} = 0. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (94)$$

Eliminating c between (92) and (93), and putting $a/b=x$,

$$90.2244(1-x) - \frac{8}{\sqrt{3}} \frac{(1+x^3)}{(1-x)^2} - \frac{24(3-x+x^3-3x^4)}{(3-2x+3x^2)^{3/2}} - \frac{24(3+x-x^3-3x^4)}{(3+2x+3x^2)^{3/2}} - \frac{8(1-x^3)}{\sqrt{3}(1+x)^2} = 0. \quad (95)$$

A graphical solution gives $x=0.515$.

$$\text{Hence } a=0.633c, \quad b=1.23c,$$

and, from (94),

$$d=5.074c.$$

$$\text{Therefore } V = -\frac{e^2}{c} \times 95.13. \quad (96)$$

The distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.096c \text{ (eight electrons),} \\ 2.13c \text{ (eight electrons),} \\ 5.074c \text{ (six electrons).} \end{array} \right\} \quad (97)$$

(ii.) *Three layers.*—Eight, twelve, and two electrons in consecutive layers, starting from the inmost. Coordinates of electrons are $(\pm a, \pm a, \pm a)$, $(\pm b, \pm b, 0)$, $(\pm b, 0, \pm b)$, $(0, \pm b, \pm b)$, $(\pm d, 0, 0)$. The distortion of the inner layers due to the presence of the two outer electrons is neglected.

$$\begin{aligned} \frac{V}{e^2} = & -22 \left[8 \left\{ \frac{1}{\sqrt{3}a} - \frac{c}{2 \times 3a^2} \right\} + 12 \left\{ \frac{1}{\sqrt{2}b} - \frac{c}{2 \times 2b^2} \right\} \right. \\ & + 2 \left\{ \frac{1}{d} - \frac{c}{2d^2} \right\} \left. \right] + \frac{8}{2} \left\{ \frac{3}{2a} + \frac{3}{2\sqrt{2}a} + \frac{1}{2\sqrt{3}a} \right\} \\ & + \frac{12}{2} \left\{ \frac{4}{\sqrt{2}b} + \frac{2}{2b} + \frac{4}{\sqrt{6}b} + \frac{1}{2\sqrt{2}b} \right\} + \frac{1}{2} \times \frac{2}{2d} \\ & + 12 \left\{ \frac{2}{\sqrt{2(b-a)^2 + a^2}} + \frac{4}{\sqrt{(b-a)^2 + (b+a)^2 + a^2}} \right. \\ & + \frac{2}{\sqrt{2(b+a)^2 + a^2}} \left. \right\} + 2 \left\{ \frac{4}{\sqrt{2a^2 + (d-a)^2}} \right. \\ & + \frac{4}{\sqrt{2a^2 + (d+a)^2}} \left. \right\} + \left\{ \frac{4}{\sqrt{b^2 + (d-b)^2}} + \frac{4}{\sqrt{2b^2 + d^2}} \right. \\ & \left. + \frac{4}{\sqrt{b^2 + (d+b)^2}} \right\}. \quad (98) \end{aligned}$$

The conditions of equilibrium, $\frac{\partial V}{\partial a} = 0$, $\frac{\partial V}{\partial b} = 0$, $\frac{\partial V}{\partial d} = 0$,

become, if a/d and b/d are neglected,

$$\frac{90.2244}{a^2} - \frac{176c}{3a^3} - \frac{24(3a-2b)}{(3a^2-4ab+2b^2)^{3/2}} - \frac{48a \times 3}{(3a^2+2b^2)^{3/2}} - \frac{24(3a+2b)}{(3a^2+4ab+2b^2)^{3/2}} = 0, \quad (99)$$

$$\frac{151.8072}{b^2} - \frac{132c}{3b^3} - \frac{24(-2a+2b)}{(3a^2-4ab+2b^2)^{3/2}} - \frac{48b \times 2}{(3a^2+2b^2)^{3/2}} - \frac{24(2a+2b)}{(3a^2+4ab+2b^2)^{3/2}} = 0, \quad (100)$$

$$\frac{43.5}{d^2} - \frac{44c}{d^3} - \frac{40}{d^2} = 0. \quad (101)$$

Eliminating c between (99) and (100), and putting $x = a/b$,

$$50.602 - 67.667x - \frac{(16-16x+36x^3-54x^4)}{(3x^2-4x+2)^{3/2}} - \frac{4(8-27x^4)}{(3x^2+2)^{3/2}} - \frac{(16+16x-36x^3-54x^4)}{(3x^2+4x+2)^{3/2}} = 0. \quad (102)$$

A graphical solution gives two values of x .

$$x = .42 \quad \text{or} \quad .809.$$

From (101), $d = 12.57c$.

$$(A) \quad x = .42.$$

Then $a = .655c$, $b = 1.56c$, $d = 12.57c$,

$$\text{and} \quad V = -\frac{e^2}{c} \times 96.50. \quad (103)$$

The distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.134c \text{ (eight electrons),} \\ 2.206c \text{ (twelve electrons),} \\ 12.57c \text{ (two electrons).} \end{array} \right\} \quad (104)$$

$$(B) \quad x = .809.$$

Then $a = .890c$, $b = 1.10c$, $d = 12.57c$,

$$\text{and} \quad V = -\frac{e^2}{c} \times 92.72. \quad (105)$$

The distances of the electrons from the atom are

$$\left. \begin{array}{l} 1.541c \text{ (eight electrons),} \\ 1.553c \text{ (twelve electrons),} \\ 12.57c \text{ (two electrons).} \end{array} \right\} \dots \dots (106)$$

Hence in this case the two inner layers have degenerated into one. It will be noticed that this model possesses a higher potential energy than either of the two others considered, and is therefore less stable.

Table showing Potential Energy and Size of Atomic Models.

Number n of Electrons.	Number of Layers.	Distances of Electrons from Atom.	Number of Electrons at given distance.	Potential Energy V.
1	1	$c \times 1.0$		$-\frac{e^2}{c} \times .5$
2	1	$c \times 1.143$		$-\frac{e^2}{c} \times 1.531$
3	1	$c \times 1.238$		$-\frac{e^2}{c} \times 2.934$
	2	$c \times 1.087$ $c \times 1.035$ $c \times 3.577$		$-\frac{e^2}{c} \times 2.787$
4	1	$c \times 1.298$		$-\frac{e^2}{c} \times 4.748$
5	1	$c \times 1.342$ $c \times 1.376$	3 2	$-\frac{e^2}{c} \times 6.806$
	2	$\times 1.273$ $\times 1.134$ $\times 5.105$	3 1 1	$-\frac{e^2}{c} \times 6.667$
6	1	$c \times 1.385$		$-\frac{e^2}{c} \times 9.40$
	2	$c \times 1.196$ $c \times 3.55$	4 2	$-\frac{e^2}{c} \times 8.868$
7	1	$c \times 1.438$ $c \times 1.370$	5 2	$-\frac{e^2}{c} \times 12.185$
	2	$c \times 1.244$ $c \times 1.191$ $c \times 4.316$	3 2 2	$-\frac{e^2}{c} \times 12.096$

Table (*cont.*).

Number n of Electrons.	Number of Layers.	Distances of Electrons from Atom.	Number of Electrons at given distance.	Potential Energy V.
8	1-(cube)	$c \times 1.446$		$-\frac{e^2}{c} \times 15.28$
	1 (twisted cube).	$c \times 1.447$		$-\frac{e^2}{c} \times 16.75$
	2	$c \times 1.105$ $c \times 3.108$	4 4	$-\frac{e^2}{c} \times 14.73$
	2	$c \times 1.312$ $c \times 1.705$	4 4	$-\frac{e^2}{c} \times 14.80$
	2	$c \times 1.287$ $c \times 1.267$ $c \times 4.80$	4 2 2	$-\frac{e^2}{c} \times 15.01$
12	2	$c \times 1.148$ $c \times 3.042$	6 6	$-\frac{e^2}{c} \times 31.2$
	2	$c \times 1.258$ $c \times 3.973$	8 4	$-\frac{e^2}{c} \times 31.8$
22	3	$c \times 1.096$ $c \times 2.13$ $c \times 5.074$	8 8 6	$-\frac{e^2}{c} \times 95.1$
	3	$c \times 1.134$ $c \times 2.206$ $c \times 12.57$	8 12 2	$-\frac{e^2}{c^2} \times 96.5$
	3	$c \times 1.541$ $c \times 1.553$ $c \times 12.57$	8 12 2	$-\frac{e^2}{c} \times 92.7$

In the case of atoms with twelve and twenty-two electrons respectively, the error in the value of the potential energy may amount to 1 per cent. In the other cases the figures are reliable only to the first place of decimals, except for atoms with one or two electrons, three electrons in one layer, four electrons, six electrons in one layer, and eight electrons at the corners of a cube, for which a more exact result is obtained, with an error of not more than .01.

It is seen from the table of results that, for values of n between 1 and 8, the potential energy is in every case less when the electrons lie in one layer than when they lie in two layers. The one-layer form of the atom will therefore

be the more stable. The difference in energy is, however, small in some cases.

Of the distributions considered when $n=12$, that in which the electrons in the layers number 8 and 4 is the more stable.

For the atom with twenty-two electrons, the first two forms possess potential energies so nearly equal that the accuracy of the calculation does not permit us to judge which is the greater. The third form is less stable.

If we consider the most stable form only for each value of n , it is shown by the following table that an empirical law,

$$\frac{V}{n(n+2)} = \text{constant},$$

holds roughly in the cases considered.

$n.$	$n+2.$	$V.$	$V/n.$	$V/n(n+2).$
1	3	$-.5 \frac{e^2}{c}$	$-.5 \frac{e^2}{c}$	$-.167 \frac{e^2}{c}$
2	4	$-1.531 \frac{e^2}{c}$	$-.765 \frac{e^2}{c}$	$-.191 \frac{e^2}{c}$
3	5	$-2.934 \frac{e^2}{c}$	$-.976 \frac{e^2}{c}$	$-.195 \frac{e^2}{c}$
4	6	$-4.748 \frac{e^2}{c}$	$-1.187 \frac{e^2}{c}$	$-.198 \frac{e^2}{c}$
5	7	$-6.806 \frac{e^2}{c}$	$-1.361 \frac{e^2}{c}$	$-.180 \frac{e^2}{c}$
6	8	$-9.40 \frac{e^2}{c}$	$-1.567 \frac{e^2}{c}$	$-.196 \frac{e^2}{c}$
7	9	$-12.18 \frac{e^2}{c}$	$-1.74 \frac{e^2}{c}$	$-.193 \frac{e^2}{c}$
8	10	$-16.75 \frac{e^2}{c}$	$-2.094 \frac{e^2}{c}$	$-.209 \frac{e^2}{c}$
12	14	$-31.8 \frac{e^2}{c}$	$-2.65 \frac{e^2}{c}$	$-.190 \frac{e^2}{c}$
22	24	$-96 \frac{e^2}{c}$	$-4.36 \frac{e^2}{c}$	$-.181 \frac{e^2}{c}$

If for $n=8$ the form possessing the greatest symmetry, *i.e.* the cube, is taken, the value obtained for $V/n(n+2)$ is $.191e^2/c$.

If the law of force between an atom and an electron is written in the form

$$\text{force} = \text{an attraction of magnitude } \frac{ne^2}{r^2} - \frac{Ne^2\alpha}{r^3},$$

where N is the atomic weight, then $c = N\alpha/n$.

Consider the distance of the electron from the atom for elements from lithium to neon, as shown in the table of results.

Element.	z .	N.	Distance of Electron from Atom.		
			$c \times 1.0$	$a \times 7$	$a \times 7$
Lithium ...	1	7	$c \times 1.143$	$a \times 5.14$	$a \times 5.14$
Beryllium	2	9	$c \times 1.238$	$a \times 4.54$	$a \times 4.52$
Boron	3	11	$c \times 1.298$	$a \times 3.89$	$a \times 3.88$
Carbon	4	12	$c \times 1.342$	$a \times 3.76$	$a \times 3.78$
Nitrogen ...	5	14	$c \times 1.385$	$a \times 3.69$	$a \times 3.69$
Oxygen	6	16	$c \times 1.438$	$a \times 3.90$	$a \times 3.80$
Fluorine ...	7	19	$c \times 1.447$	$a \times 3.62$	$a \times 3.63$
Neon	8	20			

The last column shows the values given by Sir J. J. Thomson (Phil. Mag. vol. xli. p. 524, 1921). The discrepancy which occurs in the cases of nitrogen and fluorine is due to the fact that in Sir J. J. Thomson's work the electrons are assumed to be at equal distances from the atom, whereas it is shown by the above calculations that in the equilibrium position this is not the case for these atoms. The value given in the table as the distance of the electrons from the atom is that common to the greatest number of electrons.

XI. Atom with twenty-seven electrons.

Some results of a study of an atom with twenty-seven electrons will now be given, but they can be regarded only as a first approximation to the solution.

One of the electrons is supposed to be at a distance from the atom great compared with that of the others, which have coordinates $(\pm a, \pm a, \pm a)$, $(\pm b, 0, 0)$, $(0, \pm b, 0)$, $(0, 0, \pm b)$, $(0, \pm d, \pm d)$, $(\pm d, 0, \pm d)$, $(\pm d, \pm d, 0)$, the atom being at the origin. The electrons are therefore in four layers, the outermost of which contains one electron, while the order of the others, which contain eight, twelve, and six electrons respectively, is not yet determined. The contribution to the potential energy of the system from the single electron in the outermost layer is assumed to be negligibly small.

The potential energy of the system is

$$24e^2 \times \left[\begin{aligned} & \frac{4.7217}{a} - \frac{6.3339}{b} - \frac{8.0934}{d} \\ & + \frac{c}{2} \left\{ \frac{3}{a^2} + \frac{6.75}{b^2} + \frac{6.75}{d^2} \right\} \\ & + \frac{1}{\sqrt{3a^2 - 4ad + 2d^2}} + \frac{2}{\sqrt{3a^2 + 2d^2}} \\ & + \frac{1}{\sqrt{3a^2 + 4ad + 2d^2}} + \frac{1}{\sqrt{3a^2 - 2ab + b^2}} \\ & + \frac{1}{\sqrt{3a^2 + 2ab + b^2}} + \frac{1}{\sqrt{b^2 - 2bd + 2d^2}} \\ & + \frac{1}{\sqrt{b^2 + 2d^2}} + \frac{1}{\sqrt{b^2 + 2bd + 2d^2}} \end{aligned} \right]$$

The equations necessary for equilibrium derived from this by partial differentiation with respect to a , b , and d do not admit of a solution by the methods used in the earlier part of this paper, for which it is necessary that one of the quantities a , b , or d should be negligibly small compared with one of the others—a condition which is not found to be fulfilled here.

If each layer is considered separately and its equilibrium position and potential energy found, the effect of electrons outside the layer being neglected, while those inside the layer are supposed to act as though they were all at the centre, the results given below are obtained.

Number of electrons in successive layers, proceeding outwards from the atom.			Distances of electrons in successive layers from the atom.			Potential Energy V.
6	12	8	1.066c	1.598c	4.132c	-141.0 $\frac{e^2}{c}$
12	6	8	1.177c	2.025c	4.132c	-142.6 $\frac{e^2}{c}$
6	8	12	1.066c	1.456c	3.037c	-139.9 $\frac{e^2}{c}$
8	6	12	1.10c	1.557c	3.037c	-140.3 $\frac{e^2}{c}$
12	8	6	1.177c	2.154c	5.060c	-142.9 $\frac{e^2}{c}$
8	12	6	1.10c	1.813c	5.060c	-141.8 $\frac{e^2}{c}$

The values obtained for the potential energy are seen to be nearly equal for all arrangements of the layers, so that it is not possible to determine from these results which form is the most stable.

The distance of the electron in the outermost layer is easily shown to be $27c$, and the contribution to the potential energy from it is $-.018e^2/c$.

If we take the value $-142.9e^2/c$ for V , and divide by $n(n+2)$, *i. e.* (27×29) , we find $V/n(n+2) = .183e^2/c$, a value in close agreement with those obtained above for other atoms.

My thanks are due to the Department of Scientific and Industrial Research for a grant which rendered it possible to undertake this work, and to Sir J. J. Thomson for many invaluable suggestions during its progress.

C. A *Metal Annular-Jet Vacuum Pump*. By IVOR BACKHURST, M.Sc., and G. W. C. KAYE, O.B.E., M.A., D.Sc., *The National Physical Laboratory**.

THE all-metal mercury-vapour jet-pump described in a previous paper† presents certain difficulties of construction on account of the welded joints; and accordingly a modification has been devised in which these are avoided. This is made of steel, and embodies in its design features characteristic of both the condensation and jet pump.

Description.

Fig. 1, which is drawn to scale, shows the details of the construction. As will be seen, the boiler occupies the lower third of the pump, the upper two thirds being surrounded by a water-jacket. The outer casing of the pump is made from one piece of weldless steel tube. The lower end is closed by a steel cap, which is tightly screwed on, the joint being rendered air-tight by thorough copper and nickel plating. The screwed joint between a second steel cap on the upper end and the connecting tube to the high-vacuum is similarly plated, the cap being sealed to the pump by means of wax or solder. The re-entrant projection of the connecting tube into the pump tends to check the escape of mercury vapour to the high-vacuum system.

On removing the cap, all the inner parts of the pump may

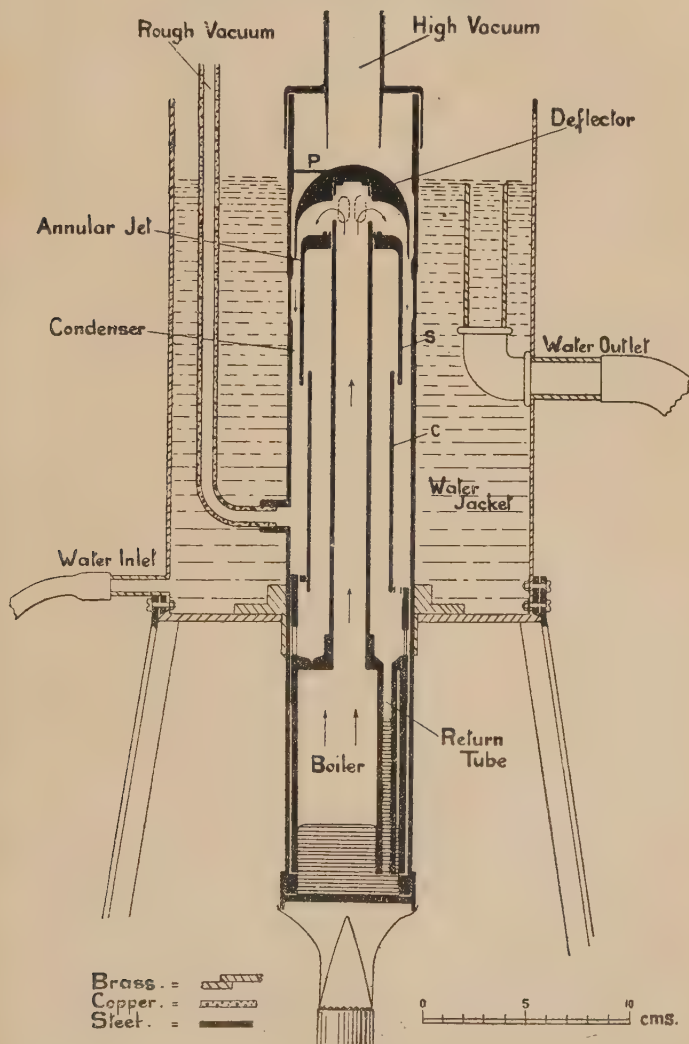
* Communicated by the Director of the National Physical Laboratory.

† Backhurst and Kaye, *suprà*, p. 918.

be lifted out together and can then be readily unscrewed apart. This construction makes cleaning exceptionally easy.

Fig. 1.

ANNULAR JET PUMP.



The deflector and sleeve S may be screwed up or down to the positions giving maximum speed over the pressure-range desired. S is fixed by means of a lock-nut (shown) and the

deflector is screwed down on to a washer (shown) of the right thickness to serve as a distance piece. When the deflector is adjusted so that its lower edge is level with the shoulder of the outer casing, the best position is obtained for general work. The curves shown in fig. 2 were obtained with the deflector in this position. Three distance pins, P, screwed into the deflector maintain it concentric with the casing.

The outer casing has two shallow grooves cut on its inner surface, one opposite the deflector, so forming a 'shoulder' for the annular jet, the other just below the jet for the purpose of increasing the efficiency of the water cooling. The amount of mercury required in the boiler is about 700 c.c. (2 lb.).

Action.

The action of the pump is as follows :—Mercury vapour from the boiler passes up the centre tube and through holes at the top to the annular space between the deflector and the sleeve S, from which it issues as a jet and entrains gas diffusing from the annular space between the deflector and the outer casing. In the region between the casing and sleeves S and C, condensation of the vapour takes place, the condensed mercury falling through the hole in C which is immediately above the return tube to the boiler. The sleeve C serves to prevent any mercury vapour which may leak from the boiler through the annular crevice and the several screwed joints just above the boiler from interfering with the vapour jet between S and the outer casing on which the pumping action depends. At the same time it prevents the condensing vapour from this jet from coming in contact with the hot central tube. Since the lower and wider part of C is in contact over an appreciable area with a water-cooled part of the outer casing, and further is separated from the top of the boiler by three pins (shown in fig. 1), it remains comparatively cold, so that the condensed mercury falling on the sloping channelled part of C is not largely re-evaporated, as would happen were it to fall directly on the top of the boiler. It is therefore possible to use a large Bunsen burner and operate the boiler at a comparatively high temperature without any likelihood of failure due to overheating. In this way the blast of vapour obtained is sufficient to supply the annular jet, which has a width of 1.75 mm. and an actual jet area of 2.85 sq. cm. On account of the greater efficiency of the annular jet compared with the circular form, much higher speeds are obtained over the usual jet-pump pressure range. At lower pressures also the pump is still able to operate,

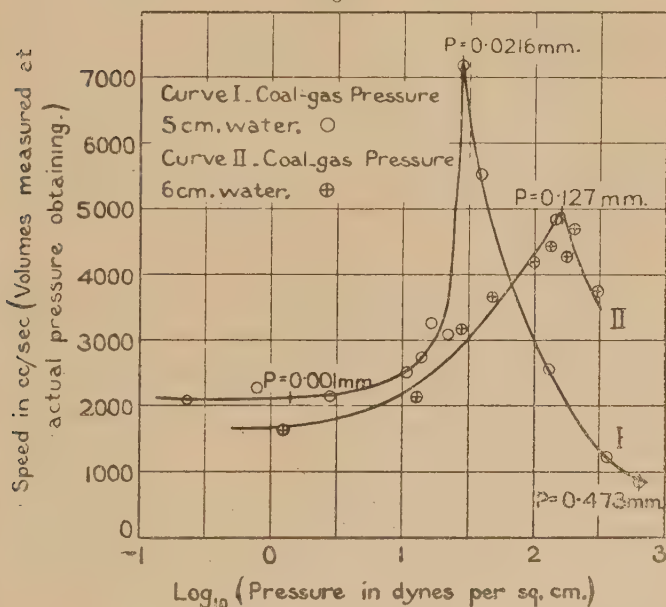
functioning then as a condensation pump, though its speed as such is necessarily restricted by the narrow width of the jet.

The pump could readily be adapted for electrical heating instead of gas.

Speed.

In fig. 2 are curves showing the way in which the speed, as defined by Gaede*, varies with the logarithm of the pressure at which the pump is working. For any particular setting of the annular nozzle the pressure at which maximum

Fig. 2.



speed is obtained depends on the working temperature of the boiler. If this temperature is increased, the maximum in general occurs at a higher pressure. Curves I. and II. were obtained, using a 1-inch diameter Meker burner supplied with gas at pressures of 5 and 6 cm. of water respectively, the general arrangement of the speed-testing apparatus employed being similar to that previously described †. In the present case the dimensions of the flow-tube for the speed tests were:—length 59.0 cm., diameter 1.0095 cm.; and of the tube connecting the latter with the pump, length 18.0 cm.,

* *Suprà*, p. 925.

† *Loc. cit.*

diameter 2.25 cm. Throughout the experiments the supporting vacuum was maintained at 0.9 mm. mercury. The speed values found using another flow tube 38.3 cm. long and 0.5077 cm. in diameter served as a check.

It will be seen from the curves that at pressures between 0.001 and 0.5 mm. mercury the speed varies between 1000 and 7000 c.c./sec., so that the pump is well suited to support a high-speed condensation pump. It is also suitable for maintaining a vacuum in a tube such as a 'gas' X-ray tube, liquid air not being required as the presence of mercury vapour does not interfere with the working of such a tube. When only moderately low pressures are required (as in the 'gas' tube), an adjustable leak of air as by a needle-valve or fine capillary is a convenient means of attaining the desired pressure.

It was found that the pump did not operate to advantage for back pressures exceeding 1 mm. mercury. Under this figure the performance of the pump, both as to speed and vacuum attained, is but little dependent on the back pressure.

Summary.

The mercury-vapour jet-pump of steel, described in a previous paper, presents certain difficulties of construction, and accordingly a modification has been devised which is without welded joints. The pump is similar to the Langmuir type, but has additional inner tubes which together with a narrow annular jet enable it to work against higher back pressures. The pump represents an attempt to combine the advantages of the jet and condensation principles in a single and readily accessible unit. Backed by an ordinary piston oil-pump, it constitutes a complete and efficient high-vacuum outfit. If mercury vapour is an objection, a liquid air trap must be employed. The pump will readily produce a vacuum of the order 0.00001 mm. mercury or less when working against a back pressure of 1 mm. mercury. The speed is high, the actual value, which varies between 1000 and 7000 c.c./sec., depending on the pressure in the vessel being exhausted, and also on the value of the back pressure against which the pump is working.

We wish to acknowledge the assistance given by Mr. J. Balmanno and Mr. W. H. Sewell, of the Observer Staff of the Laboratory.

The investigation was carried out in part in connexion with work for the Radio Research Board of the Department of Scientific and Industrial Research.

CI. *The Electronic Theory of Valency*.—Part IV. *The Origin of Acidity*. By Prof. T. MARTIN LOWRY, C.B.E., M.A., D.Sc., F.R.S.*

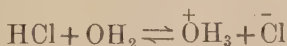
THE object of this communication is to unite into one definite hypothesis a number of suggestions which have been made in earlier papers of this series, and elsewhere, as to the nature of acids and the origin of acidity.

1. *The Nature of Acids.*

An acid may be defined as *a hydride from which a proton can be detached, e.g. on dissolution in an ionizing solvent, on electrolysis, or by displacement by a metallic ion*. This definition † appears likely to hold its own, in spite of proposals that would either restrict its scope ‡, by limiting it to the hydrates of anhydro-acids §, or broaden it to include compounds not containing any hydrogen ||. Thus, although it is true that water is needed to make hydrogen chloride conduct, this does not prove that water is a necessary constituent of an acid, since it may only mean that the proton always seeks out an alternative resting-place when it is threatened with eviction from an acid, and that, if alternative accommodation is not provided, it may refuse to be displaced. In other words, the ionization of an acid may be, not a dissociation as expressed in such an equation as



but a double decomposition of the type



There is therefore no need to narrow the definition of an acid by confining it to compounds which contain oxygen as well as hydrogen. On the other hand, there are real advantages in maintaining the positive relationship between acidity

* Communicated by the Faraday Society.

† Compare *Chemistry and Industry*, xlii. p. 43 (1923).

‡ *Ibid.* p. 46.

§ Werner, 'New Ideas,' 1911, p. 212; compare *Chemistry and Industry*, xlii. p. 1048 (1923).

|| G. N. Lewis, 'Valence,' 1923, p. 142.

and the presence of a proton which is indicated in the definition set out above, in place of widening this definition so as to include any substance which can make away with a hydroxyl ion, or even with another anion, such as a fluoride ion.

2. *The Development of Acidity.*

When the hydrides of the lighter elements are compared, a very remarkable contrast is observed between successive members of a series such as CH_4 , NH_3 , OH_2 , FH , Ne . Thus the monohydrides FH , ClH , BrH , IH are amongst the strongest acids; but SH_2 is already a very weak acid and OH_2 is commonly regarded as neutral. Ammonia is more of a base than an acid, since it is more ready to take up a proton as in NH_4^+Cl^- than to lose one as in NaNH_2^+ . In methane, acidic and basic properties have both disappeared, the former on account of the greater stability of this hydride as compared with NH_3 or OH_2 , the latter on account of the fact that the octet of carbon cannot carry any more radicles beyond the four hydrogen atoms which are already attached to it in methane. In the first paper of this series* I suggested that this progressive disappearance of acidity was not due directly to change of valency, but that it might be associated much more closely with the growing size of the molecule which had been demonstrated by the experiments of Rankine† on the collision-areas of these molecules as deduced from measurements of the viscosity of the gases. This suggestion is repeated in a more precise form in the following paragraph.

3. *Bohr's Atom in Relation to the Problem of Acidity.*

Although the brilliant investigations of Bohr have led at present only to a theory of the structure of free atoms and ions, it is already possible to surmise the direction in which developments must take place in order that it may provide in due course a working hypothesis of the structure of molecules also. In particular, the view is now widely accepted that the "shared electrops" of the static models must be translated into "shared orbits"‡ in the dynamic model of the

* Trans. Faraday Soc. xviii. p. 292 (1923); Phil. Mag. xlv. p. 1116 (1923).

† Trans. Faraday Soc. xvii. p. 719 (1922).

‡ Niessen, Dissertation, Utrecht, 1922; Pauli, *Ann. d. Physik*, lxviii. p. 177 (1922); Campbell, *Nature*, cxi. (Apr. 28, 1923); Fowler, Trans. Faraday Soc. xix. p. 461 (1923); Sidgwick, *ibid.* p. 469.

molecule. In the recent discussion on "The Electronic Theory of Valency" I suggested * that the development of looped orbits may be related in a very simple manner to the well-known relativity effect. In a free atom or ion this gives rise to precession of the orbit; but the intersection of the inward and outward paths, which is the main feature of this effect, is exactly what is needed in order to produce a figure-of-eight orbit enveloping two nuclei. Since the major axis of an orbit is inversely proportional to the effective nuclear charge, it is clear that the size of the loop must be smaller in FH with a nuclear charge of 9 than in CH_4 with a nuclear charge of 6, in complete qualitative agreement with the observations of Rankine. It is not easy to say what relationship will exist between the size of the looped orbit and the magnitude of the force with which it binds together the two nuclei which it encloses; but the repulsion between them must certainly increase rapidly as the two nuclei are brought more closely together by the contraction of the loop. From this point of view it appears that the four hydrogens of methane may be held securely by looped orbits, with the focus of the outer loops at a considerable distance from the nucleus; whereas the much smaller loop in which the proton of hydrogen fluoride is held must bring it nearer to the nucleus, and may easily bring it so near that it can be driven outside the loop by the strong repulsion to which it is subjected.

4. Transmission of Acidity.

It is of interest to reconsider, in the light of the views set out in the preceding paragraph, the mechanism by which acidity is propagated in a chain of atoms, *e.g.* from Cl to H in $\text{Cl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{OH}$. When a static model is used, the simplest mechanism is that suggested by Langmuir †, namely a displacement of the nuclei relatively to the enveloping shells of electrons. When a dynamic model is used, this conception becomes of less utility, since it is difficult to imagine that the orbits can be diverted very much from their normal course round the nucleus—at any rate in the inner portion of the path. It is therefore more reasonable to suppose that, since an orbit with a chlorine-nucleus in one focus is necessarily of smaller dimensions than a corresponding orbit containing a carbon nucleus, the dimensions of a looped orbit which contains chlorine in one focus and carbon in the other will

* Trans. Faraday Soc. xix. p. 480 (1923).

† Trans. Faraday Soc. xvii. p. 609 (1922).

be intermediate in size between those of binuclear orbits containing either two chlorine or two carbon atoms. It is moreover reasonable to think that the contracted orbits of a chlorine atom may tend to impose a like contraction on orbits of similar quantum-number in an adjacent carbon atom when some of these orbits are shared by both atoms. This effect, transmitted in a diminished degree as the length of the chain is increased, would account for the "general effect" of acylous and basylous radicles, as illustrated by the tables in Part III. of this series of papers.

It will be noticed that this effect is always in the same direction. It has been suggested that, in the transmission of acidity through a chain of atoms, an alternating effect (basylous, acylous, basylous, acylous, etc.) is sometimes produced in consecutive atoms; but, as I have already stated, I am not yet convinced that there is any sufficient experimental basis for this view.

5. *Summary and Conclusions.*

(a) The increasing acidity of the hydrides from CH_4 to FH or from SiH_4 to ClH is attributed to a progressive diminution in the size of the orbits of the electrons by which the protons are linked to the central nucleus.

(b) It is suggested that acylous atoms such as chlorine tend to diminish the size of the orbits of electrons which they share with another atom, and that this effect can be transmitted to other orbits of the same quantum-number in the latter atom. In this way the transmission of acidity through a chain of atoms can be interpreted by means of a dynamic, instead of a static, model. Conversely, basylous groups must expand the orbits of electrons which they share with other atoms.

(c) From this point of view an unsubstituted hydrocarbon chain should act as a neutral radicle in carboxylic acids, since orbits shared by two carbon atoms will be of normal dimensions. Hydrogen directly attached to an atom of sulphur, phosphorus, etc., is more acylous than an alkyl radicle because it allows for a greater contraction of the orbits; but even a proton is less acylous than the "lone pairs" of electrons in acids such as FH and ClH , since contraction is probably at a maximum in orbits which are entirely unshared.

CII. *On the Emission of Positive Ions from Hot Tungsten.*
By Professor W. A. JENKINS, University of Dacca,
India.*

DURING an investigation upon the alteration of resistance of a tungsten spiral when emitting electrons, it was observed that when the temperature of the spiral reached a certain value a further increase in the temperature resulted in a decrease of the electron current. It has been known for some time that there is a maximum to the current available with a fixed voltage, and that beyond a certain point an increase of temperature does not result in an increase of the electron current. This phenomenon has generally been attributed to the existence of space-charge; but while it is possible to explain the existence of a saturation value by means of the space-charge hypothesis, it does not seem easy on this theory to account for a decrease of the current. More detailed experiments upon the magnitude of the electron current at a high temperature showed that the phenomenon of a decrease of the electron current with increase of temperature was not reproducible with all the tungsten wires used. These experiments, in which a more sensitive galvanometer than usual was employed, revealed the fact that at about the temperature at which the electron current reached a maximum value or commenced to decrease, an emission of positive ions began. This positive current could be observed, of course, by reversing the potential used for the observation of the electron current. The present paper is an account of investigations carried out upon this positive ion emission at high temperatures.

It has long been known that in the presence of gas most metals emit positive ions at fairly low temperatures; but this phenomenon is one which varies enormously under different conditions and which disappears with the elimination of the gas. When a metal is heated in vacuo, and the temperature is not allowed to vary, the emission of positive ions which is great at first gradually diminishes until it is too small to measure. After continued heating in a vacuum, a metal ceases to emit positive ions, but its power may be restored by treating it in one of several ways †.

In addition to this effect, characteristic of new wires heated in a vacuum, it is found that the introduction of almost any gas will cause the production of both positive and negative ions.

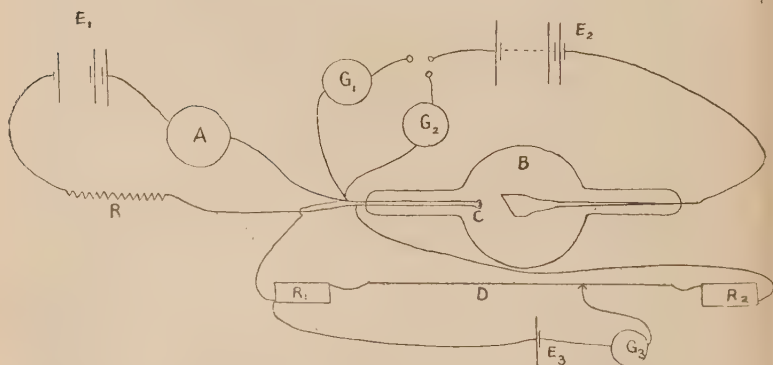
* Communicated by the Author.

† Richardson, 'Emission of Electricity from Hot Bodies,' pp. 202-204.
Phil. Mag. S. 6. Vol. 47. No. 281. May 1924. 3 U

These ions are heavy and are not affected by weak magnetic fields. Richardson and Chaudhuri* have shown that the use of a magnetic field when the driving voltage is small can be used as a criterion of the absence of gas and the formation of ions by collision. According to their experiments a tube can be regarded as satisfactory, *i. e.* free from gas and the wire sufficiently glowed out, when a transverse magnetic field will entirely prevent the electron current from passing between electrodes 2 cm. apart with a driving potential of several volts. In any tube in which there are traces of residual gas, or in which the wire retains traces of occluded gas, the application of a magnetic field will not entirely prevent the electron current from passing. This residual current is attributed to the formation of ions by collision. The positive emissions discussed in the present paper are of an entirely different character, however, from those which have been previously observed.

Apparatus used.

Fig. 1.



E_1 is a battery of twelve 2-volt accumulators used for heating the tungsten spiral in the Coolidge tube B. The current through the tungsten spiral was measured by the ammeter A, and could be varied through wide limits by means of the resistance R.

E_2 is a battery which varied in different parts of the experiment from 2 volts to 220 volts.

G_1 is a galvanometer used for measuring the positive electron current.

* Phil. Mag. Feb. 1923, p. 337.

G_2 is a high sensitivity galvanometer used for measuring the positive emission current.

E_3 is a 2-volt accumulator used in combination with the galvanometer G_3 , the resistances R_1 and R_2 , and the potentiometer wire D for accurately measuring the drop in potential between the terminals of the tungsten spiral. It was found that the ordinary connexions of the Coolidge tube were not sufficiently good to allow of a balancing point on the potentiometer being obtained. Thick copper leads were therefore soldered to the terminals of the spiral after the ordinary connecting cap had been removed. This considerably improved the steadiness of the current through the spiral, and enabled the potential fall between the terminals to be accurately determined.

The Coolidge tube was placed between the poles of a powerful electromagnet, so that the space between the cathode and the anticathode was in the central part of the field. The pole-pieces were, of course, widely separated, but with a current of about $5\frac{1}{2}$ amperes a field of approximately 400 was obtained.

A Coolidge tube is not an ideal form of apparatus for the experiments in question, but for preliminary work it offers many advantages. The vacuum is very high and the spiral is thoroughly glowed out, so that although the tubes used had been employed for X-ray work for several months, a discharge could not be passed through them when the tungsten spiral was cold. The application of the tests employed by Richardson and Chaudhuri for the absence of gas, either residual or occluded, also showed that the tubes were in a satisfactory condition for the experiments. Below a temperature of about 2500°C . there were no positive ions present in the tubes. Further, when a magnetic field of strength 400 was applied at right angles to an electron current flowing under a driving potential of less than 10 volts, the electron current was entirely stopped, even when the current flowing was as high as 3×10^{-4} ampere, the temperature over 3000°C ., and a galvanometer of sensitivity 4×10^{-10} employed.

If voltages greater than 10 were employed, the magnetic field was insufficiently strong to prevent completely the electron current from passing between the electrodes. This is what one would expect, for the velocity of the electrons increases with the driving potential. Whatever effects are observed, therefore, may be presumed to be pure emission effects, unaffected either by the presence of gas within the tube or occluded gas within the spiral.

General Description of the Phenomena observed.

The tungsten spiral was heated in the ordinary manner, and the current gradually increased. At first the discharge was a pure electron discharge following the curve already investigated by many physicists. When the current through the spiral reached a certain value, however, the electron current ceased to increase, and a further increase of the heating current generally resulted in a slight diminution of the electron current. Up to just below this point no positive emission could be detected, even with an applied voltage of over 200 and a very sensitive galvanometer. Further increase of the heating current gave rise to a positive emission, which increased rapidly with the temperature. This positive emission current also varied with the applied voltage—with time—with the previous treatment of the spiral and with the application of a magnetic field. These variations are not simple, and will be described in detail. In order to obtain accurate measurements of this positive emission current, which was generally very small, it was necessary to eliminate all leakage currents. With 24 volts on the heating circuit, 200 volts on the positive emission circuit, and a different 200 volts on the electromagnet circuit some trouble was experienced with insulation. This was eventually overcome by using nothing but air wires (except for the electromagnet) and by placing each individual piece of apparatus upon separate blocks of paraffin-wax. In addition, it was found necessary to place the cells used upon separate tables, and to stand these tables upon blocks of either ebonite or paraffin-wax. Even with these precautions it was not possible to obtain satisfactory readings immediately after a shower of rain when the atmosphere was moist. During the rainy season in Bengal, experiments of this kind are out of the question.

Variation of the Emission with the Temperature.

Keeping the applied voltage constant, experiments were carried out with different tubes, and the results set forth in Table I. obtained. The voltage used was 220, this being the maximum available. In all cases the values shown are the maximum ones obtained neglecting the initial discharge, which will be dealt with later in the paper. The temperatures were not measured directly, but were deduced from the values of the resistance obtained from the current and the potential determinations. For this purpose the data given in Langmuir's paper were used.

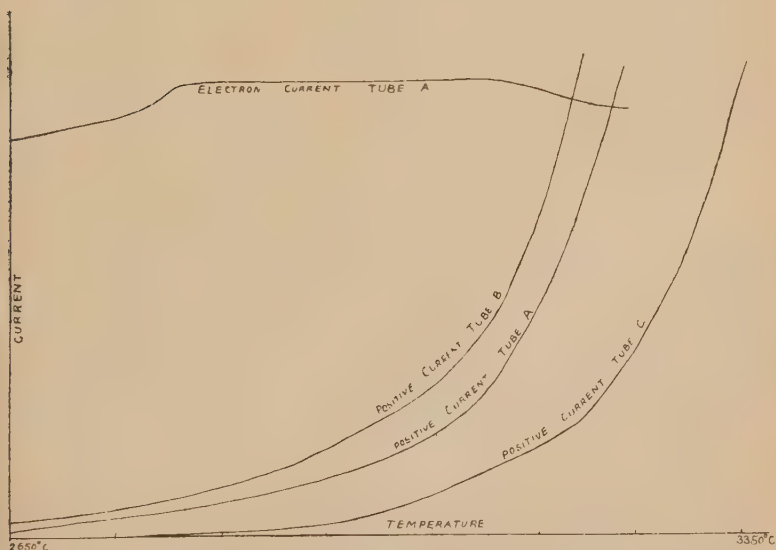
* Langmuir, *Physical Review*, vi. (1915).

Table I. shows a complete set of data for experiments carried out with the first tube. The results obtained with

TABLE I.

Heating Current.	Resistance (spiral).	Temperature.	Electron Current.	Positive Current.
5.85 amperes.	2.410	3500° C.	79×10^{-5} amp.	370×10^{-8} amp.
5.4 "	2.226	3270	81 "	100 "
5.3 "	2.186	3210	82 "	63 "
5.2 "	2.144	3160	87 "	39 "
5.1 "	2.095	3100	87 "	23 "
5.0 "	2.049	3040	87 "	16 "
4.85 "	1.947	2920	87.5 "	9 "
4.75 "	1.904	2870	87.5 "	6 "
4.65 "	1.872	2830	87 "	6 "
4.55 "	1.843	2790	82 "	4.8 "
4.45 "	1.810	2750	79.5 "	4.8 "
4.35 "	1.777	2710	78.5 "	3.6 "
4.25 "	1.744	2670	77 "	2.4 "
4.15 "	1.711	2620	76 "	2.4 "
4.05 "	1.672	2580	75 "	1.2 "
3.95 "	1.640	2540	74 "	0 "
3.85 "	1.616	2520	72 "	0 "
3.6 "	1.521	2400	66 "	0 "

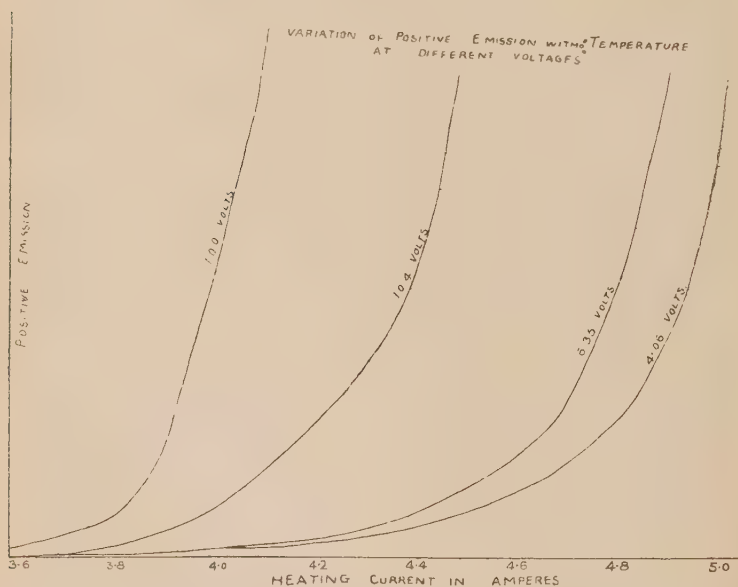
Fig. 2.



other tubes were similar, and are shown in graph form in fig. 2.

It will be observed that the positive currents obtained with the third tube used, *i. e.* tube C, are much smaller than those obtained with the other two tubes. This tube also gave much smaller electron currents than did either of the other two. That the positive discharge does not begin with tube C until a temperature of nearly 2800 C. has been reached is probably due to the fact that below this temperature the emission was so small that the galvanometer used was not capable of detecting it. The scale used for plotting the electron current is, of course, a different one from that used for plotting the positive current. The curves are of similar shape, as is shown

Fig. 3.



in fig. 3, but the magnitudes less when driving voltages of less than 220 volts are used. In the case of these latter voltages, however, the values of the positive emission obtained when a magnetic field is applied must be used in order to get the true emission effect. The reason for this will be discussed later.

It is unlikely that in a Coolidge tube the whole of the emitted particles, whether electrons or positively-charged particles, reach the anticathode, especially when the voltage is small. The conformation of the tube prohibits this, and it is therefore not possible to deduce from the above results

any definite relationship that may exist between the temperature and the positive emission. All that it is possible to say is that as the temperature increases from 2500°C. to the melting-point, the emission increases very rapidly. The largest positive emission observed was 5.9×10^{-6} ampere. This was obtained with the first tube, which also gave the greatest currents, and showed no maximum electron emission even with the highest temperatures used. With more suitable forms of tubes in which the emitting wire is entirely surrounded by a receiving electrode, it should be possible to obtain saturation values of the emission current at voltages much less than 220. Such values would enable one to deduce the relation between the temperature and the positive emission. It is proposed to continue the investigations upon these lines.

Variation of the Emission with the Driving Voltage.

Table II. and fig. 4 show the characteristic features of the variation of the emission with the applied voltage up to a maximum of 220 volts. It will be seen that the emission rises uniformly with the voltage up to 16 volts, and then apparently approaches a saturation value. On further increasing the voltage the emission very considerably increases. It is possible that at the higher voltages the potential assists in pulling out the positive particles as well as increasing the velocity. This point also can be more satisfactorily decided in an apparatus in which the whole of the emitted particles are collected on the receiving electrode. For purposes of comparison the variation of the electron current with the applied voltage is also shown.

The results indicate that the electron current increases uniformly with the voltage, and this suggests that the lack of uniformity which marks the variation of the positive current with the voltage is a general phenomenon, and is not due to the asymmetrical shape of the Coolidge tube. If this is so, it is clear that there is some cause operating at the higher voltages which is not present at the lower ones. The table shown is one of many that were obtained using different values of the heating current.

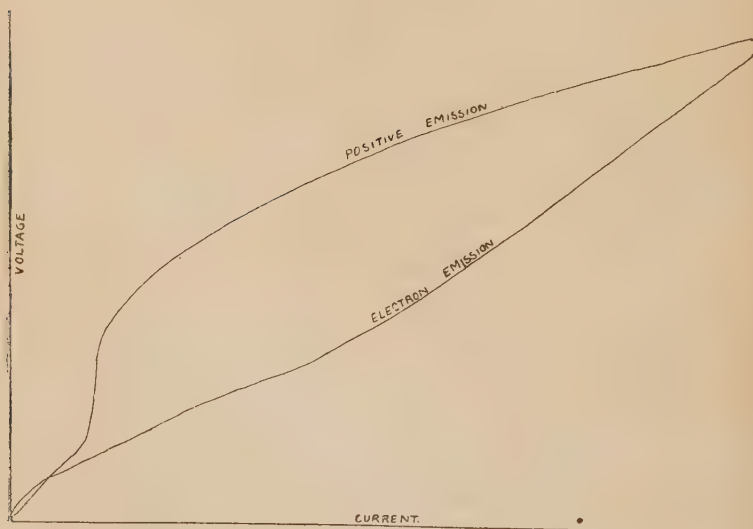
Variation of the Emission with the Magnetic Field.

Table III. shows the values of the electron current obtained for different values of the heating current when different driving voltages were used and a magnetic field of

TABLE II.

Heating Current.	Voltage.	Electron Emission.	Positive Emission.
4.6 amperes.	0	63×10^{-8}	0
	2.08	19×10^{-6}	24×10^{-10}
	4.25	80	56
	5.84	130	80
	7.95	227	104
	10.06	320	132
	12.16	458	160
	14.28	528	192
	16	662	212
	20	732	224
	28	1308	232
	34	1580	240
	50	2200	400
	100	3840	2080
	220	12660	5400

Fig. 4.



strength 400 Gauss was applied. In conformity with the results of Richardson and Chaudhuri, if the applied voltage be less than 10, the magnetic field entirely destroys the electron current: but if the heating current be large, *i. e.* if the temperature of the wire be high, then the application of a magnetic field not only destroys the electron current, but

it results in the appearance of a small current flowing in the opposite direction. There appear to be two possible sources for this current. It may either be an electron current flowing from the anticathode to the cathode, or it may be a positive emission current flowing from the heated spiral to the anticathode. The former would be of the nature of a photoelectric current caused by the incidence of ultra-violet light upon the tungsten anticathode. This cannot be ruled out at once as an impossibility, for it must be remembered that the spiral is at a very high temperature and is emitting intense light, and, further, that the vacuum in the tube is extremely high. The latter condition would permit of very short waves reaching the anticathode before being absorbed.

TABLE III.

Current.	2.06 Volts.	4.06 Volts.	6.35 Volts.	8.45 Volts.	10.4 Volts.	25 Volts.	50 Volts.
3.8.	0	0	0	0	0	6 L	84 L
4.1.	0	0	0	0	0	36 L	135 L
4.4.	3 R	0	0	0	0	480 L	720 L
4.65 ...	13 R	0	0	0	160 L	560 L	1120 L
4.8.	22 R	1 R	0	0	175 L	600 L	1440 L
5.0.	38 R	5 R	0	0	180 L	720 L	1752 L
5.1.	824 L	2184 L
5.2.	11 R	1 R	0			
5.4.	20 R	3 R	0			

It is not probable, however, that the velocity of electrons emitted as a result of photoelectric action would be sufficiently high to allow of the electrons reaching the heated spiral against the applied potential, and in spite of the magnetic field. Moreover, experiments show that at higher temperatures there is a definite positive emission when the applied voltage is such as to aid in their emission. It seems unnecessary, therefore, to bring in any other hypothesis to account for the phenomena in question than that the current is due to positive charges emitted from the heated spiral and possessing sufficient velocity to overcome small negative potentials, tending to keep them within the heated spiral. The variation of the magnitude of this small positive current

with the temperature of the wire and the applied potential bears out this view. The current is greatest with the highest temperature and the smallest voltage, decreases rapidly as the voltage increases, and becomes zero at even the highest temperature when the applied voltage is 8. This means that the velocity of the positively-charged particles, which are otherwise free to come out, is too small to overcome a restraining potential of 8 volts.

With an applied voltage of 2.06 volts the electron current is entirely stopped even at very high temperatures, and the positive ions overcome the adverse potential of 2.06 volts without difficulty. At 4.06 volts two causes may operate or partially prevent the positive ions from manifesting themselves. In the first place, the potential of 4.96 volts may be sufficient to stop some of them getting across, and secondly, at the higher temperature some of the electrons may possess sufficient velocity to get across in spite of the magnetic field. The former is the more likely reason, for when an applied voltage of 8.45 is used there is no current at all when the magnetic field is put on. It is extremely unlikely that at all the higher temperatures the residual electron current and the positive current will exactly counterbalance each other; so that one must infer that with this applied voltage the electrons have still insufficient velocity to get across when the magnetic field is applied, while the voltage is high enough to prevent all the positive ions from getting across. At higher potentials, as the table shows, some of the electrons get across in spite of the magnetic field.

The R denotes that the deflexions were to the right and a positive current was flowing. L denotes that an electron current was flowing. Table IV. shows the variation of the positive emission with a magnetic field under different conditions. The results as regards magnitude of emission are not absolutely consistent, probably owing to the experiments having been carried out on different days. It is not easy to reproduce exactly any given condition of the tube, and it is by no means certain that exactly the same results would be obtained at different times, even if the conditions were exactly reproduced. The essential features of the phenomena were, however, always reproduced, and considering the nature of the experiments, the results are as consistent as could be expected. When the applied potential was low, the positive emission current increased considerably with the application of the magnetic field. This means that a certain number of electrons were able to reach the anticathode in spite of the adverse potential. The positive emission appeared to be smaller, therefore, than it really was. On switching on the

magnetic field, these electrons were deviated under the joint influence of the magnetic field and the applied potential, and the full positive emission was observed. This increase is more noticeable with the smaller applied voltages than with the large ones, as one would expect. With the highest voltages used, the effect disappeared altogether at the lower temperatures; but at the higher temperatures the reverse effect appeared, *i. e.* the positive emission current showed an unmistakable decrease when the magnetic field was applied. This means that some of the particles carrying charges were either sufficiently light or moved sufficiently slowly to be affected by a field of 400 gauss.

TABLE IV.

Variation of Positive Emission with Magnetic Field.

Current.	2.06 Volts.		4.06 Volts.		6.35 Volts.		8.45 Volts.		10.4 Volts.	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
3.5	0	0	0	0	0	0	0	0	0	0
3.75	0	0	0	0	0	1	0	2	0	2
4.0	1	10	2	9	3	4.5	5	13	18	22
4.25	4	16	5	18	10	24	16	29	61	156
4.5	6	40	13	41	23	50	28	54	250	300
4.75	20	114	46	111	145	202	80	140	1140	1710
5.0	86	220	213	453	520	843	175	804	3060	3390
5.1	780	1260	315	600		
5.25	630	1200	690	1200		

Current.	25 Volts.		50 Volts.		100 Volts.		220 Volts.	
	A.	B.	A.	B.	A.	B.	A.	B.
3.5	0	0	0	0	8	8	30	30
3.75	0	2	0	1.5	29	29	55	55
4.0	7	13	6	10	50	50	360	300
4.25	45	57	62	70	1050	840	740	660
4.5	255	260	267	280	3300	2760	2400	2050
4.75	1270	1170	2070	2120	6240	5250	4200	3810
5.0	3090	2550	3660	3840	7200	6840		
5.1	6300	4650	5700	5850				
5.25	16500	14400

The figures under column A indicate deflexions obtained when no magnetic field was applied. Those under B indicate deflexions obtained when the magnetic field was applied.

There is no evidence as yet of the existence of positive electrons of mass comparable with that of the negative electrons, and one must therefore conclude that some of the positively-charged particles moved with velocities considerably less than those of the negative electrons. The velocity of the emitted positive particles will, of course, increase with the applied potential, and one would expect the effect of the magnetic field to be greater when the lower voltages are used. Any effect of this kind, however, is completely masked at the lower voltages by the fact that negative electrons are able to flow across against the applied potential. It is possible also that when higher voltages are applied, positively-charged particles are torn from the cathode, and that these particles move with a much lower velocity than those which are spontaneously emitted. Fig. 3, showing the variation of emission with voltage, suggests such an effect.

Variation of the Initial Emission with the Previous Treatment of the Spiral.

During the course of the experiments it became apparent that the magnitude of the initial deflexion obtained at any given temperature and applied voltage varied according to the previous treatment of the spiral. If the positive potential were applied before the spiral was heated, then, on heating the spiral, the deflexion remained at zero for some time, depending on the temperature of the spiral, and then gradually rose to its normal value. This was not due to the spiral's requiring a considerable period for attaining its final temperature, for similar experiments with the electron current indicated that the final temperature was quickly attained. Fig. 5 illustrates this phenomenon.

It will be seen that, while the electron current has attained 96 per cent. of its final value 15 seconds after the commencement of the heating and its maximum value after one minute, the positive emission does not begin until after 30 seconds have elapsed, and it does not attain its maximum value until the potential has been applied for approximately 3 minutes. As indicated in fig. 6, this period is longer when the applied voltage is small, but even with an applied voltage of 220 there is no emission during the first 30 seconds. In a Coolidge tube the application of a positive potential of 220 volts would not entirely prevent the emission of electrons, but it would very considerably diminish the outflow.

Fig. 5

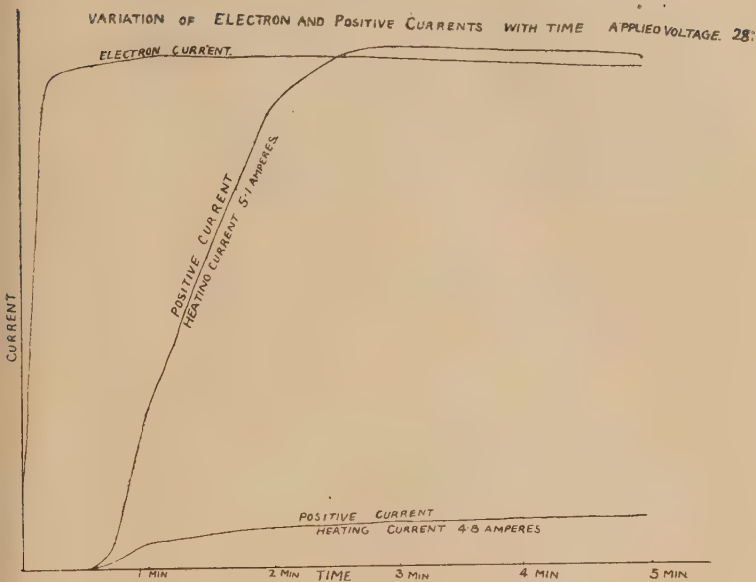
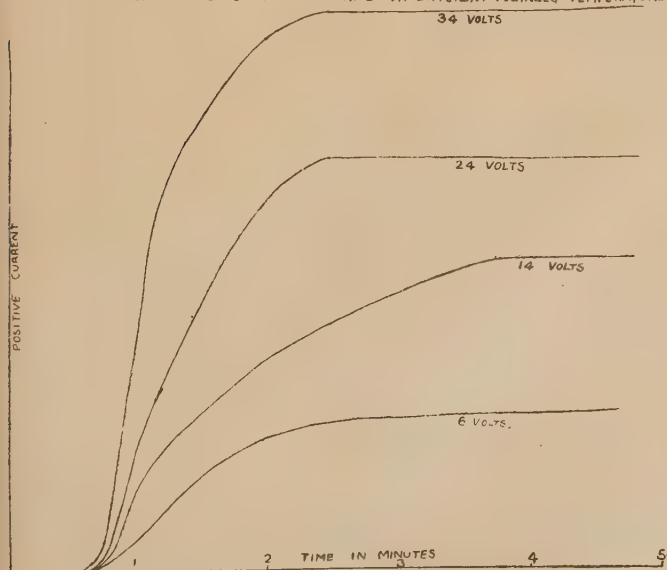


Fig. 6.

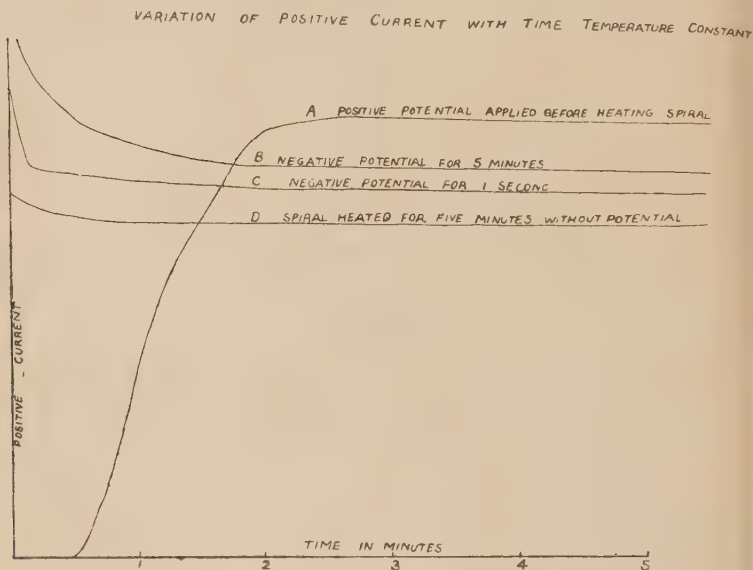
VARIATION OF CURRENT WITH TIME AT DIFFERENT VOLTAGES TEMPERATURE CONSTANT.



A considerable time would therefore elapse before the spiral had lost sufficient electrons to make the wire strongly electro-positive. When this condition was attained positive emission would be easier.

It is possible that even at the high temperatures at which the emissions take place there would be no positive emission unless the heated filament were discharging negative electrons. This point will be tested in experiments that are to be carried out with filaments surrounded by cylindrical electrodes.

Fig. 7.



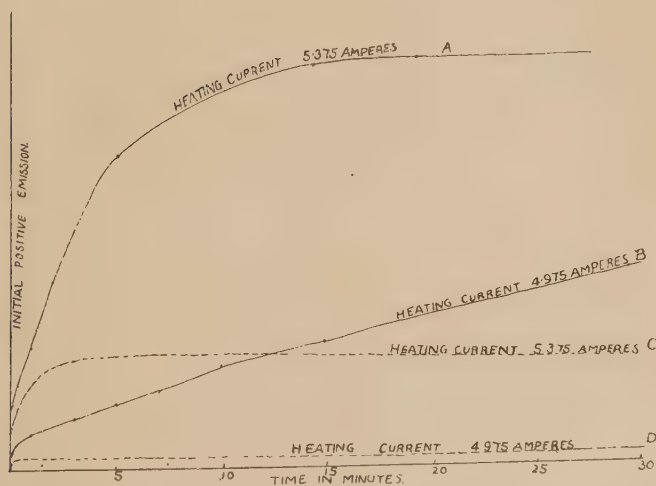
That the emission of electrons in large quantities prior to the positive emission measurements facilitates the discharge of positive electricity is shown clearly in figs. 7 and 8.

Fig. 7 shows the different types of curves that are obtained when the condition of the heated spiral prior to the measurements varies. Curve A is the normal type of curve obtained when the positive potential is applied to the spiral before the heating current is turned on. As described previously, the emission does not begin until after 30 seconds have elapsed, and the maximum is not reached until about three minutes have passed. Curve B shows the type of curve that is obtained when, instead of applying the positive potential before the spiral is heated, the spiral is first heated

and a negative potential assists the discharge of negative electrons for a period of five minutes and then the positive emission measurements are made. Here, instead of the initial positive emission current being zero, it is too great to measure with the galvanometer used, and remains above its normal value for a period of almost two minutes. Curve C is similar, the negative potential here being applied for a period of one second before taking the positive readings. Curve D shows the results obtained when the spiral is heated

Fig. 8.

VARIATION OF INITIAL EMISSION WITH TIME ELECTRON CURRENT
HAS BEEN FLOWING PREVIOUS TO MEASUREMENT OF POSITIVE EMISSION



for five minutes, but no potential is applied prior to the taking of the measurements of the positive emission. It will be noticed that here also there is a larger than normal value at first. The fact that the normal value of the emission gets gradually less in the four curves is due to the fact that the heating current in the spiral was gradually diminishing and its temperature therefore decreasing.

Fig. 8 illustrates more clearly the actual magnitudes of the initial emissions under the different conditions. In this graph the initial emission is plotted against the time that the spiral had been heated before the initial emission was measured. Curves A and B are for two different temperatures when, during the preliminary heating, the emission of

electrons was assisted by a negative potential of 220 volts. The dotted curves C and D are for similar temperatures when no potential at all was applied during this preliminary heating. It will be observed that in curves C and D a saturation value of the initial kick is soon reached, and that prolonged heating does not give rise to any further increase in the initial emission. This does not appear to be the case in curves A and B, and not only are the corresponding deflexions much larger than in C and D, but there appears to be no limit to the value of the initial kick, at any rate within the limits of the readings taken. For example, when the heating current was 4.975 amperes and the normal value of the positive emission a deflexion of 16 divisions, an initial deflexion of over 900 was obtained when a negative potential had been previously applied for a period of $2\frac{1}{2}$ hours. Moreover, not only was there a large discharge of positive electricity immediately after the long period of emission of negative electrons, but the deflexion did not fall down to its normal value for over an hour. It should be stated that the final steady value of the emission was independent of the initial condition. The fact that a saturation value is reached in curves C and D is probably explained by the fact that when no potential is applied the spiral will at first discharge negative electrons, but after a time the discharge will cease, owing to the spirals having attained a certain positive potential which will prevent further emission. There will be no such cessation of electron discharge when a negative potential is applied to the spiral.

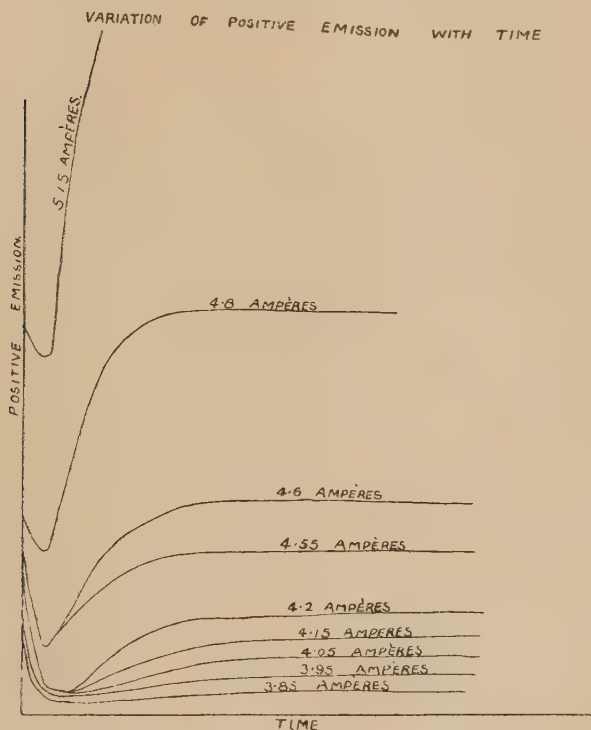
Fig. 9 shows the variation of the emission with time at different temperatures when the spiral had been heated for a few seconds only prior to the application of the positive potential.

It will be seen that in all the curves the emission drops to a minimum value after about 15 seconds and then rises to its normal value. The previous curves do not show this phenomenon, owing to the fact that the galvanometer in use was not sensitive enough to reveal it. When the more sensitive galvanometer was employed it was always observed.

It was thought at first that the initial emission might be due to the return of the space-charge to the heated spiral, but experiments upon this point negatived the idea. If, under the conditions of the experiment, the accumulated space-charge were sufficient to give a large kick to the galvanometer upon the application of a positive potential, then, if the heating circuit of the spiral were broken and the positive potential immediately applied, a similar kick should

be observed. Experiments on these lines, however, showed that the kick due to space-charge was not observable. One must assume, therefore, that the continued negative emission causes the accumulation of large positive charges upon the spiral, which are immediately expelled upon the application of a suitable potential. An alternative explanation is that the continued heating and emission of negative

Fig. 9.



electrons causes the expulsion of occluded gases ; but this does not seem to explain the phenomenon as well as the former hypothesis.

It is interesting to note that continuous positive emission over a period of 18 hours does not result in either prolonged increased negative emission or a large initial negative emission.

The following table of successive readings of the two.

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currents illustrates the different behaviour with regard to this phenomenon:—

	Initial Emission.	Steady Value.
1. Negative Emission	0	100
2. Positive Emission taken after the negative current had flowed for 20 seconds	37	6
3. Negative Emission taken after the positive current had flowed for 6 hours	0	98
4. Positive Emission taken after the electron current had flowed for 2½ hours.....	256	6
	After 1 min. 40	

In the last reading the steady value was reached after a period of 13 minutes. In interpreting these tables it must be remembered that the electron emission is of a different order entirely from the positive emission, and that while the behaviour with regard to percentage changes is undoubtedly different in the two cases, an effect of the actual magnitude of the positive effect would hardly be observable when measuring the electron current. The reason why after large initial emission the discharge falls well below its normal value is not clear, and it is proposed to carry out further experiments upon this point.

Another matter of great importance is the value of the emission after what has so far been called the steady state has been reached. From the experiments carried out it has not been possible to ascertain whether prolonged emission results in a decrease in magnitude of the emission. The evidence tends to show that there is such a decrease with time, but exactly what is the rate of this decrease has not as yet been determined. With a Coolidge tube the currents required for heating the spiral to a high temperature are considerable, and in the case of the highest temperatures are well over 5 amperes. A slight diminution of current results in an appreciable decrease of temperature, and this is associated with a considerable diminution of positive emission. For accurate results it is necessary, therefore, to keep the heating current constant over long periods of time. Cells giving out a current of 5 amperes over a period of from 6 to 24 hours run down appreciably, and it is not easy to arrange for resistance to be cut out at such a rate as to keep the current absolutely constant. Periodic alterations of resistance are not satisfactory, as sudden alterations of temperature of the spiral, even though these changes be minute, cause anomalous and erratic results. Filaments which require a much smaller heating current will be better adapted

for experiments upon this point. The following tables show the type of results that have so far been obtained:—

TABLE V.

Approx. Current.	Applied Voltage.	Time.	Deflexion.
4.65	10.38	0	69
4.65	10.38	1 hr. 40 min.	63
4.65	10.38	2 hr. 30 min.	60
4.6	34	0	62
4.6	34	6 min.	61.75
4.6	34	10 "	63.5
4.6	34	15 "	63.5
4.6	34	23 "	64
4.6	34	30 "	61.5

In all experiments carried out the emissions followed the same curve. When the positive potential was applied before the spiral was heated, the emission gradually rose from zero to a maximum value, and thereafter apparently decreased very slowly with the time.

This maximum value is the value that has hitherto been called the steady value, as, in the case of all except the highest temperatures, it is by no means certain that the subsequent decrease is any greater than can be accounted for by the decrease in value of the heating current. In the above table the time zero is the time when this maximum value was reached.

If, however, the temperature be near the melting-point of tungsten, the positive emissions are very large, and there is undoubtedly a rapid decrease of the emission with the time, as is shown in Table VI. The values of the emission have

TABLE VI.

Approx. Current Heating.	Applied Voltage.	Time.	Deflexion.
5.85 amperes.	200	0	9300
5.85 "	200	3 min.	6300
5.85 "	200	6 "	5250
5.85 "	200	10 "	4350
5.85 "	200	15 "	3525
5.85 "	200	20 "	2910
5.85 "	200	30 "	2115
5.85 "	200	40 "	1605
5.85 "	200	60 "	1065
5.85 "	200	75 "	810
5.85 "	200	90 "	630
5.85 "	200	175 "	150

been adjusted so as to be on the same scale as in the preceding table.

With reference to the above table, it should be stated that, when after nearly three hours' heating the positive emission had decreased to the value shown, it was observed on reversing the potential that the electron current was very small, and immediately afterwards the spiral burnt out. Experiments upon prolonged emissions of both electrons and positive charges at temperatures near the melting-point would probably prove fruitful, but with Coolidge tubes would be rather an expensive proposition.

The Nature of the Positive Emission.

There seems to be little doubt that the current observed when a positive potential is applied to the spiral is due to the emission from the tungsten of particles carrying a positive charge.

It was suggested to me at first that the current might be due to photoelectric effect, the electrons being liberated from the tungsten anticathode by the incidence of the intense light emitted from the heated cathode. Such a photoelectric effect would, of course, increase rapidly with the temperature of the spiral.

The effect of the magnetic field upon the magnitude of the current and the experiments upon the growth of the current with time when the potential is applied before the spiral is lit up, rule out this explanation of the phenomenon. If it were a photoelectric effect, then the application of a magnetic field would probably destroy the current altogether, and, even if it did not destroy it, would certainly considerably diminish it. The general effect of the magnetic field is to cause an increase of the current at small potentials and a slight decrease at larger potentials and higher temperatures. This slight decrease at the higher temperatures may be owing to the fact that at these temperatures a small portion of the current is due to photoelectric action. Again, if the effect were photoelectric in origin, the rate of increase of the current with time would follow the curve of increase of temperature of the spiral. As soon as the maximum temperature was attained, the current would also reach a maximum, and would remain constant as long as the temperature of the spiral remained constant. The experiments with the electron currents show that the final temperature is reached after an interval not much greater than 15 seconds, whereas in some cases the maximum value of the positive current is not

attained until 6 minutes have elapsed. Further, the large initial emissions obtained after the spiral has been heated for some time or after the electron current has been flowing, would be difficult of explanation on the photoelectric hypothesis unless one assumes the presence of occluded gases within the spiral.

The obvious explanation of positively-charged particles emitted from the heated tungsten seems to be capable of accounting for all the phenomena observed. Even at the highest temperatures the number of these positive charges is only a small fraction of the number of negative electrons emitted, and until these electrons are prevented from passing between the electrodes, the current carried by the positively-charged particles cannot be observed. A high positive potential or a combination of a low positive potential and a magnetic field serves to eliminate the electron current, and leaves the positively-charged carriers open to observation.

If this explanation is the correct one, it is important that the nature and the origin of these positively-charged particles should be ascertained. With the apparatus available it was not possible to measure the deviation of these particles under the influence of a magnetic field, beyond observing that a field of 400 was not sufficient to prevent their passing between the electrodes. This points to the fact that the particles are either very heavy- or very slow-moving, or possibly a combination of the two. Previous work * on the production of ions from hot bodies indicates their existence (a) when there is residual gas in the apparatus or occluded gas in the metal, (b) when the metal is freshly heated in vacuo. These ions, however, are not positively-charged ions of the heated metal, although Thomson † has obtained evidence of the existence of positively-charged atoms of platinum emitted from heated platinum.

The present experiments reveal phenomena of an entirely different character from any previously observed. There is practically no residual gas in the tube, nor, so far as one can tell, is there occluded gas within the tungsten. The emission does not commence until a temperature of approximately 2500° C. is reached, and, so far as the writer is aware, this is considerably higher than in the case of previous experiments upon positive emission. Tungsten is, of course, the only common metal that can be heated to such a temperature, but it is possible that careful experiments upon metals at

* Richardson, 'Emission of Electricity from Hot Bodies,' pp. 196-250.

† Thomson, 'Conduction of Electricity through Gases,' 2nd ed., p. 220.

temperatures not far removed from their melting-point might reveal phenomena of a similar character. The positive emissions in the present experiments are affected by, and seem to be bound up with, the emission of large quantities of negative electrons. Unless one assumes that the electrons emitted are surplus atmosphere electrons moving about in the interatomic spaces, one must conclude that the emission of large numbers of negative electrons will leave behind positively-charged atoms of tungsten. At high temperatures there will be a tendency for these positively-charged atoms to evaporate and leave the metal. A suitable potential will assist this evaporation. It is known that at temperatures not far removed from the melting-point tungsten is surrounded by an atmosphere of tungsten vapour, for the spectrum shows reversed lines. The dragging away of these vapour atoms or molecules if they happened to be positively charged would, of course, be easy. The phenomena are not, however, due to normal evaporation alone, as the peculiar behaviour under prolonged observation indicates. The large initial emissions also point to a more complicated origin. After prolonged heating with a high negative potential applied, one might expect a large supply of positively-charged atoms both on the surface and within the metal.

The application of a positive potential would remove all the surface positively-charged atoms immediately, and for a considerable period there would be an abnormally large current, the length of the period being dependent upon the length of time the heated metal had been emitting large quantities of negative electrons. Afterwards a normal value should be reached. In the apparatus used the application of a high positive potential, although preventing the passing of electrons between the electrodes, would not prevent entirely the emission of electrons from the heated tungsten. In an apparatus where the heated filament was totally surrounded by the electrode and the application of a positive potential would prevent altogether the emission of electrons, it is possible that the positive emission would be either stopped or greatly diminished.

All the phenomena seem to be explicable upon the hypothesis that positively-charged atoms or molecules of tungsten are emitted from the heated spiral. The fact that a magnetic field of 400 gauss diminishes the emission slightly at the highest temperatures probably indicates that a small percentage of the particles are moving very slowly. A photoelectric effect at these high temperatures seems

improbable if the heated tungsten is surrounded by an atmosphere of vapour, for this atmosphere N would absorb any very short wave-lengths and prevent any light, that would be likely to give the observed effect, from reaching the anticathode. One must assume, then, the presence of very slow-moving positively-charged particles as well as faster-moving ones. The only alternative is to assume the existence of positively-charged electrons; and as there is no evidence as yet of the existence of these, this hypothesis is not a desirable one.

Summary.

(1) It has been observed that at temperatures approaching its melting-point, tungsten emits positively-charged particles.

(2) These particles are probably atoms or molecules of tungsten.

(3) A magnetic field of 400 gauss only affects a small percentage of them.

(4) The magnitude of the emission of these positive charges increases rapidly with the temperature.

(5) If the heated tungsten previous to observation for positive emission emits large quantities of negative electrons, there is a large initial emission of positively-charged particles when the potential is reversed.

(6) The positive emission is of a different order from the electron emission, being much smaller.

(7) At the highest temperatures the positive emission decreases rapidly with time, but at moderate temperatures the decrease with time, if existent at all, is small.

(8) Certain tubes showed a diminution of the electron current near the point where the positive emission began. Others did not.

In conclusion I wish to express my thanks to Mr. Phanindra Nath Mitra for valuable help given in the carrying out of the experiments.

CIII. *The Entrainment of Air by a Jet of Gas issuing from a Small Orifice in a Thin Plate.* By J. S. G. THOMAS, D.Sc. (Lond. and Wales), A.R.C.Sc., A.I.C., Senior Physicist, South Metropolitan Gas Company*.

IN previous communications† particulars have been given of an experimental investigation of the discharge of air and other gases at various temperatures through a small orifice in a thin plate, and the entrainment of air by the jet of issuing gas. In particular it was shown that in the case of a lighter gas issuing into a heavier gas, the degree of air entrainment effected per unit volume of gas issuing in the jet was dependent both upon the density of the issuing gas and that of the air into which the gas issued. The experimental results were satisfactorily explained both qualitatively and quantitatively by assuming that the entrainment was effected in part as the result of a process of the nature of diffusion of the lighter issuing gas into the surrounding atmosphere. Thus it was shown that the volume V of air entrained (reduced to N.T.P.) per unit volume of gas issuing in the jet (measured under the experimental conditions of temperature and pressure) was given by

$$V = \alpha [\rho_1 + \beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{1/2}],$$

where α is the volume of air entrained by a jet of air of standard density, taken as the unit, issuing at the same excess pressure as the gas into air of equal density, β is the diffusion constant, and ρ_1 and ρ_2 denote respectively the density of the issuing gas and that of the gas into which the jet issues. The present communication deals with the dependence of the ratio V/α and hence of β upon certain of the experimental conditions, more especially upon the degree of restriction, by orifices or otherwise, of the amount of air entrained by the jet issuing under any specified excess pressure, and upon the diameter of the orifice through which the jet issues.

EXPERIMENTAL.

The apparatus corresponded very closely with that described in the latter of the two previous communications‡. The only essential differences were that the discharge tube (A) and the tube (D) into which the discharge issued were of

* Communicated by the Author.

† Phil. Mag. xlv. p. 969 (1922); xlv. p. 785 (1923).

‡ Phil. Mag. xlv. p. 785 (1923). The letters in the text refer to the figure given on p. 786 (*loc. cit.*).

somewhat smaller diameter than those specified therein, whilst the tube (E) through which air was induced by the jet was somewhat shorter.

The manner—if any—of the dependence of the value of the ratio V/α upon the degree of restriction of the air induced by the jet of gas was investigated by determining the amounts of air respectively induced by jets of air and hydrogen issuing from a specified orifice. The total amount of air induced was satisfactorily and easily varied by inserting brass diaphragms having different sized orifices in the induction tube (D). A few experiments were in like manner carried out with coal gas discharged through the jet orifice. These served to confirm results obtained with air and hydrogen. For the purpose of investigating the dependence, if any, of the value of the ratio V/α upon the diameter of the jet orifice, experiments were likewise carried out with a number of the jet orifices described in a previous paper*. The methods of experiment and deduction of results have already been sufficiently described. The temperature of the discharge was maintained constant at 13° C. to within $\pm 0.5^\circ$.

RESULTS AND DISCUSSION.

(1) *Character of the Aeration Curves relating Entrainment of Air to Pressure at the Jet Orifice.*

Curves representative of the results obtained when orifices of various diameters were inserted in the induction tube so as to restrict to a greater or less degree the amount of air induced by a jet of air or of hydrogen are shown in fig. 1, in which some of the experimental points have been omitted for clearness. Particulars referring to the diameter of the orifices so inserted and other details are given in Table I. The respective values of V/α were calculated from the experimental results as previously explained†.

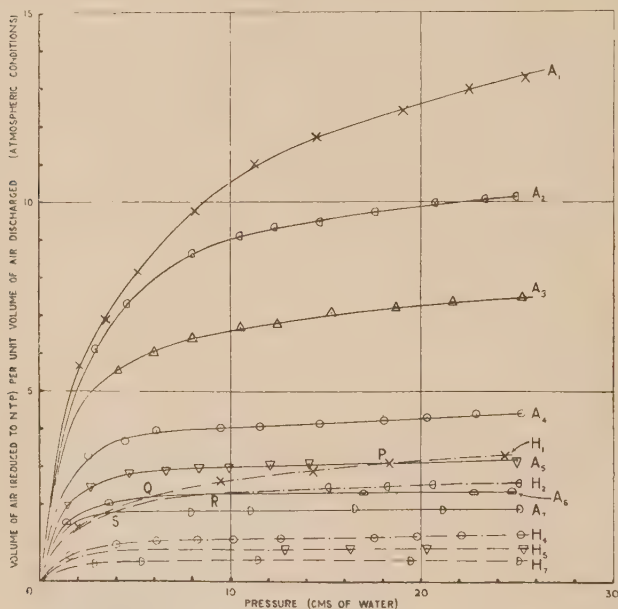
Referring to the curves A_1 to A_7 in fig. 1 relating to air entrainment by a jet of air issuing at various pressures, it is seen that as the degree of possible entrainment is restricted by the insertion of a smaller orifice in the induction tube, the aeration of the jet increases less rapidly with pressure, until in the case of curve A_7 the aeration of the jet is constant throughout the range of pressures 4 cm. to 25 cm. of water. This result is in marked contrast to the result indicated by curve A, representing results obtained with the

* Phil. Mag. xlv. p. 969 (1922).

† Phil. Mag. xlvi. pp. 792, 793.

open induction tube, which is typical of results contained in the two previous papers of this series. The manner in which the respective curves in their main portions increasingly approach to parallelism with the axis of pressures as the size of the orifice in the induction tube is reduced, is clearly seen from the respective values of the ratio of the aerations effected by the jet at pressures equal to 25 cm. and 2 cm. of water. For the series A_1 to A_7 , these values are respectively 2.42, 1.98, 1.67, 1.47, 1.43, 1.36, and 1.23. A corresponding result holds in the case of the curves H_1 to H_7 referring to

Fig. 1.



air entrainment by a jet of hydrogen. It would appear therefore that a constant or approximately constant value of the aeration at different pressures characterizes a flow system in which induction of air is effected under conditions such that the flow of the stream of air induced by the jet is considerably reduced from its normal value in free air either by restricting the effective area of the induction tube or otherwise. The results contained in Technologic Paper No. 193 (1921) of the Bureau of Standards relating to the design of atmospheric gas burners are of this character, and it would appear from what has been said, and from a consideration of the experimental method employed for

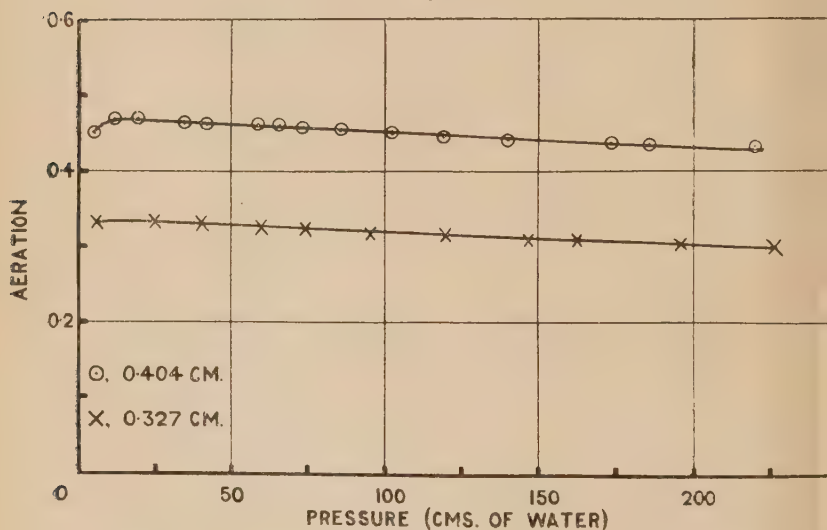
TABLE I.
Diameter of Orifice through which Jet of Gas issues 0.0607 cm.

No. of disk inserted in induction tube.	Diameter of orifice in disk in induction tube (cm.).	Total volume of air (measured at N.T.P.) induced by air discharged at excess pressure 25 cm. of water (A) (c. ft. per hour).	Total volume of air (measured at N.T.P.) induced by hydrogen discharged at excess pressure 25 cm. of water (H) (c. ft. per hour).	Ratio $\frac{H}{A}$	Mean ratio V/a (from curves).	β .
1 (open tube)	2.025	24.1	20.9	0.87	0.253	0.713
8	1.911	23.9	20.9	0.88		
9	1.812	23.8	20.8	0.87		
10	1.714	23.0	20.2	0.88		
11	1.572	22.1	19.4	0.88		
12	1.496	21.0	18.4	0.88		
13	1.379	19.2	17.5	0.91		
2	1.271	17.6	16.5	0.94	0.257	0.724
3	1.023	12.9	12.7	0.98	0.265	0.740
4	0.763	7.6	7.68	1.01	0.270	0.769
5	0.634	5.48	5.54	1.01	0.274	0.770
6	0.544	4.04	4.20	1.04	0.276	0.797
7	0.482	3.19	3.37	1.06	0.285	0.824

measuring the air induced, that the results contained in that Paper are not applicable to conditions such as hold in the case of the operation of by far the greater proportion of atmospheric gas-burners, in which aeration is effected by the jet under what may be briefly referred to as "free induction" conditions, the minimum restraint consistent with the prevention of back-firing being imposed upon the induced stream of air.

It is of interest to examine the character of the aeration curves at higher values of the pressures at the jet. For this purpose experiments were carried out with coal gas discharged at pressures up to about 230 cm. of water through a circular orifice 0.1019 cm. diameter in a disk of thickness

Fig. 2.



0.265 cm. The induction tube was restricted by the insertion of an orifice of diameter either 0.327 cm. or 0.404 cm. The gas discharged through the orifice was measured by means of a high-pressure gas-meter made by Sugg, and was dried by passage over calcium chloride. The results obtained are briefly indicated in fig. 2. The ordinates represent the respective volumes of air (measured at N.T.P.) entrained per unit volume of coal gas in the jet, measured at atmospheric temperature and pressure. It will be noticed that at the comparatively high pressures employed in these experiments the degree of aeration of the jet decreased slightly and linearly as the pressure at the jet orifice was increased. The aeration of high-pressure jets will be discussed in more detail in a later paper.

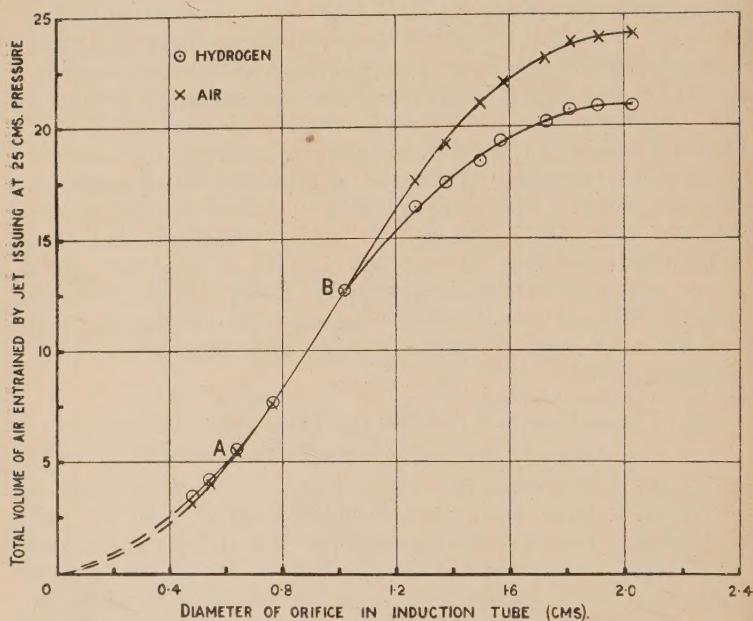
One other characteristic of the curves in fig. 1 may be referred to here, as it illustrates the difficulty experienced in the practical application of the results of aeration experiments carried out under specified conditions. Referring to curves H_1 and A_5 in fig. 1, the former relating to entrainment of air by a jet of hydrogen, no restriction being inserted in the induction tube, whilst the latter refers to entrainment of a jet of air issuing through the same orifice, the induction tube being restricted, it will be noticed that whereas for pressures at the jet less than about 19 cm. of water (see point P, fig. 1) the jet of air effects the greater degree of air entrainment per unit volume of the jet, for pressures above this amount the jet of hydrogen effects the greater degree of aeration. Similar crossing of curves relating to jets of hydrogen and air are seen at Q, R, and S. It is therefore clear that conclusions relating to aeration of jets of different gases operating at various pressures under different conditions as regards size of the induction tube cannot be drawn from results based upon observations made at a single value of the pressure.

(2) *Dependence of V/α upon the Degree of Restriction of the Amount of Air induced by the Jet.*

In fig. 3, experimental results given in columns 2 and 3 of Table I. have been plotted respectively as abscissæ and ordinates. The curve so drawn represents the dependence of the total volume of air entrained by a jet of air issuing under an excess pressure equal to 25 cm. of water through an orifice of diameter 0.0607 cm., upon the diameter of the orifice restricting air flow in the induction tube. A similar curve is drawn for a jet of hydrogen from the data contained in columns 2 and 4 of Table I. It will be seen that for values of the total volume of air entrained by the respective jets ranging from about 6.5 to 10 cubic feet per hour (see points A and B, fig. 3) the volumes entrained are practically equal in the case of the two gases. For greater values of the total entrainment, however, the air jet is the more effective, whilst for smaller values the hydrogen jet is more efficient. The maximum difference in the total entrainments effected by the respective gases under the conditions of the experiments amounts to only 13 per cent., which is small compared with the ratio of the respective densities of the two gases. We have in a previous paper ascribed the air-entraining power of a light gas issuing into a denser gas in part to diffusion of the issuing light gas into the denser surrounding atmosphere. The present result suggests that this process of diffusion of hydrogen occurs to

an increasing degree either as the *total* volume of air entrained by the jet under a specified pressure is reduced, or alternatively as the volume of air entrained *per unit volume* of the jet discharged under a specified pressure is diminished.

Fig. 3.



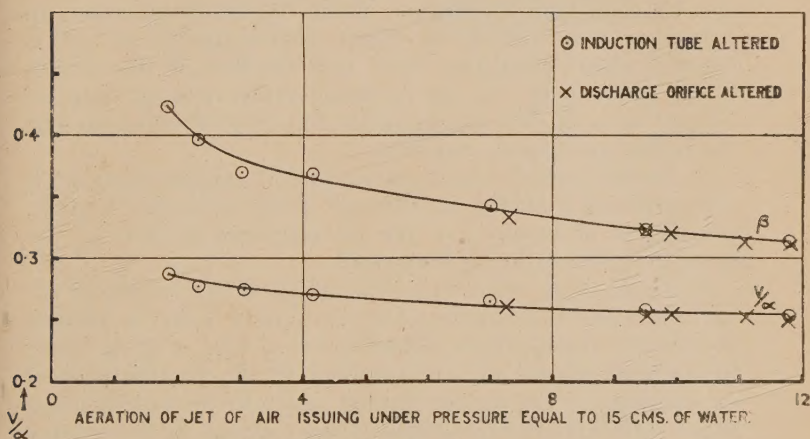
In fig. 4 the values of V/α contained in the sixth column of Table 1. have been plotted as ordinates against the respective volumes of air entrained *per unit volume* of air issuing from an orifice of diameter 0.0607 cm. under a pressure of 15 cm. of water. (This pressure was chosen in order that the results might be compared with later results in which the size of the orifice was altered.) The abscissæ in fig. 4 therefore serve to indicate the relative restriction of the effective diameter of the induction tube produced by the insertion of the various disks referred to in column 2 of Table 1. Values of β have been calculated from the respective values of V/α by means of the equation

$$V/\alpha = \rho_1 + \beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{1/2},$$

account being taken of the temperature and pressure of the issuing gas and of the surrounding atmosphere at the time of the experiment. The values of V/α and β so determined are indicated by the symbol \odot in fig. 4. The experimental values under which these values were

obtained were such that a *decrease* of the *total volume* of air entrained by the jet issuing under a specified pressure accompanied a decrease of the air entrained *per unit volume* of the jet. Results in which a *decrease* of the *total volume* of air entrained by the jet issuing under a specified pressure was accompanied by an *increase* in the volume of air entrained *per unit volume* of the jet are indicated by the symbol \times in fig. 4. These latter results were obtained by the use of jets issuing through orifices of different sizes. We have previously shown* that a diminution in the size of the orifice through which a jet issues effects, under a specified excess pressure, a smaller total air entrainment but a greater air entrainment per unit volume of the jet. We see in fig. 4

Fig. 4.



that all the experimental points lie fairly well on a smooth curve, indicating an increase in the value of V/α and in the value of β as the aeration *per unit volume* of the jet issuing under a specified pressure decreases. We conclude therefore that in all cases the process of diffusion of hydrogen into the surrounding denser atmosphere occurs to an increasing degree as the aeration of the jet per unit volume under a specified pressure diminishes, irrespective of whether the decreased aeration is accompanied by an increase or decrease of the total volume of air entrained by the jet under the specified pressure. An increase in the value of β , *i.e.* in the diffusion effect, might be anticipated when the effective surface per unit volume of the jet is increased by diminishing the diameter of the orifice through which the jet issues. The results afforded by the present series of

* Phil. Mag. xlv. p. 984 (1922).

experiments indicate that the curves through the respective series of points (represented by \odot and \times) are coincident within the limit of experimental error so that the magnitude of any such possible effect is in any case small compared with the increase attributable to a decrease of the aeration per unit volume of the jet under a specified pressure as explained above. It is interesting to note that extrapolation of the upper curve in fig. 4 indicates that when the aeration of the jet is reduced to zero, the value of β is approximately unity.

SUMMARY.

1. It is shown that a constant or approximately constant value of the aeration of a jet of gas issuing at different pressures from an orifice, as referred to in Technologic Paper No. 193 (1921) of the Bureau of Standards, characterises an induction flow system in which the induction of air is effected under conditions such that the flow of the stream of air induced by the jet is considerably reduced from its normal value in free air by restricting the effective area of the induction tube or otherwise.

2. In the case of a gas issuing under comparatively high pressures and inducing air through a restricted flow system, the degree of aeration of the jet decreases slightly as the pressure at the orifice is increased.

3. In all cases, whether a diminution of the volume of air entrained per unit volume of a jet issuing under a definite pressure is accompanied either by a decrease or an increase in the total volume of air entrained by the jet, the process of diffusion of the lighter issuing gas into the surrounding denser atmosphere occurs to a greater degree as the volume of air entrained per unit volume of the jet diminishes. The results obtained indicate the very approximate equality of such increased diffusion effect derived whether from a decrease in the effective surface per unit volume of the jet or by reducing the effective diameter of the inductive flow system.

The experimental work detailed herein was carried out in the Physical Laboratory of the South Metropolitan Gas Company, and the author desires to express to Dr. Charles Carpenter and the Directors his thanks for the ready provision of all facilities necessary for carrying out the work.

Physical Laboratory,
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709 Old Kent Road, S.E. 15.
5 March, 1924.